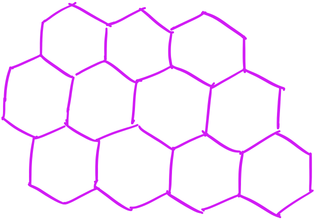
SiC Final Cell Issue

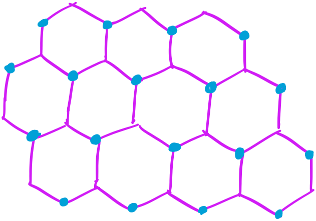
Saturday, May 31, 2025 10:36 AM

verify that the region with possibility for pathological 5-ring is unavoidable

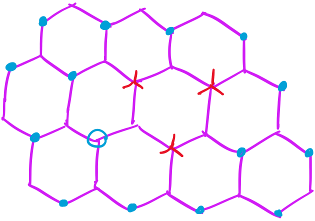
schematic of SiC(111) surface



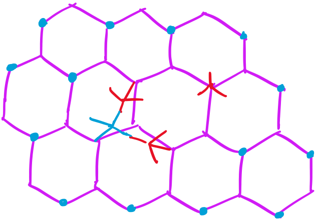
annotating Si bridgehead sites on flat surface



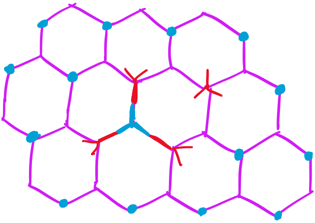
methyl protective groups before 1st cage



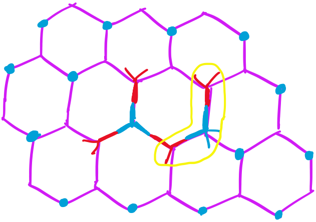
critical 5-ring for 1st cage



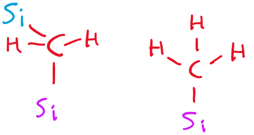
completion of 1st cage



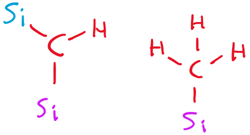
formation of next 6-ring



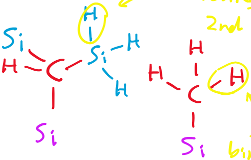
1)


Si
H
C
H
Si
H
H
C
H
Si

2)


Si
C
H
Si
H
H
C
H
Si

3)


Si
H
C
Si
H
Si
H
H
H
H
C
H
Si

binding energy: −4.75 eV
2nd removal: −3.03 eV

binding energy: −5.47 eV

testing alternative means to derive a binding energy

$C_3Si-SiH_2$ −1.99 eV C_3Si-CH_2 −4.38 eV

$C_3Si-SiH_3$	−3.10 eV	C_3Si-CH_3	−4.38 eV
H binding	−4.58 eV	H binding	−5.47 eV

C_3Ge-CH_2	−3.71 eV	H	−10.71 eV
C_3Ge-CH_3	−3.59 eV	CH_3	−96.95 eV
H binding	−5.48 eV		

looks too complicated; try interpolation

$(R_2CH-CH_2)_3C-CH_3$	−5.66 eV	
$(R_2\underbrace{Si}_{\text{change to C}}H-SiH_2)_3C-CH_3$	$\boxed{-4.96\text{ eV}}$	closest estimate
$(R_2CH-CH_2)_3Si-CH_3$	−5.47 eV	
$(R_2SiH-SiH_2)_3Si-CH_3$	−5.07 eV	

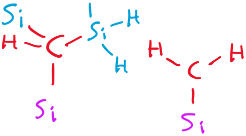
$(R_2CH-CH_2)_3C-SiH_3$	−4.85 eV	
$(R_2\underbrace{Si}_{\text{change to C}}H-SiH_2)_3C-SiH_3$	$\boxed{-4.75\text{ eV}}$	closest estimate
$(R_2CH-CH_2)_3Si-SiH_3$	−4.58 eV	
$(R_2SiH-SiH_2)_3Si-SiH_3$	−4.47 eV	

branch: H does/doesn't tunnel from Si to C

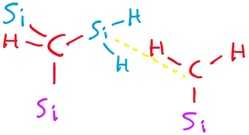
does not tunnel (simulations suggested this)

H

4)


Si
H
C
Si
H
H
Si
H
C
H
Si

5)

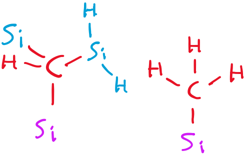

Si
H
C
Si
H
H
Si
H
C
H
Si

concerted mechanism

H abstraction near-instantly forms Si–C

does tunnel

4)

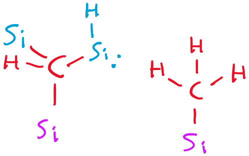

H
Si
H
C
Si
H
Si
H
H
C
H
Si

don't remove from CH_3 because nondeterministic outcome

(1) Si–C forms

(2) H tunnels from Si to C

5)


H
Si
H
C
Si:
Si
H
H
C
H
Si

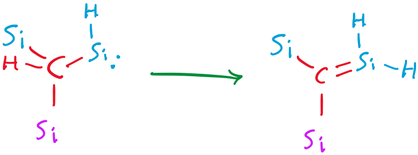
use C_3Sn tool if unable to positionally constrain the hydrogens of SiH_2.

$Si_3C-SiH_2 \longrightarrow Si_3C-SiH + H$ 3.03 eV

$C_3Sn-H \longrightarrow C_3Sn + H$ 3.29 eV

C_3Sn has little chance of ripping of the Si

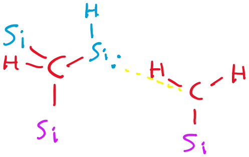
unexplored pathology


Si
H
H
C
Si
Si
H
Si
C
Si
H
Si

if it does happen, can be guaranteed to happen 100% of the time by waiting long enough

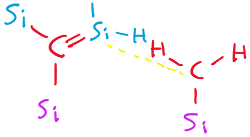
pi bond doesn't form:

6)


Si
H
H
C
Si
Si
H
C
H
Si

pi bond does form:

6)

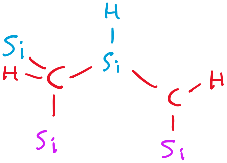

Si
Si
H
H
C
C
H
Si
Si

use HAbst tool pointing sideways to avoid reacting with Si group

3DOF but requires plurality of tips

pi bond doesn't form:

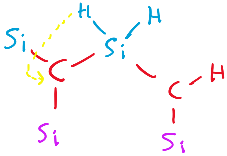
7)


H
Si
Si
H
C
C
H
Si
Si

pi bond does form:

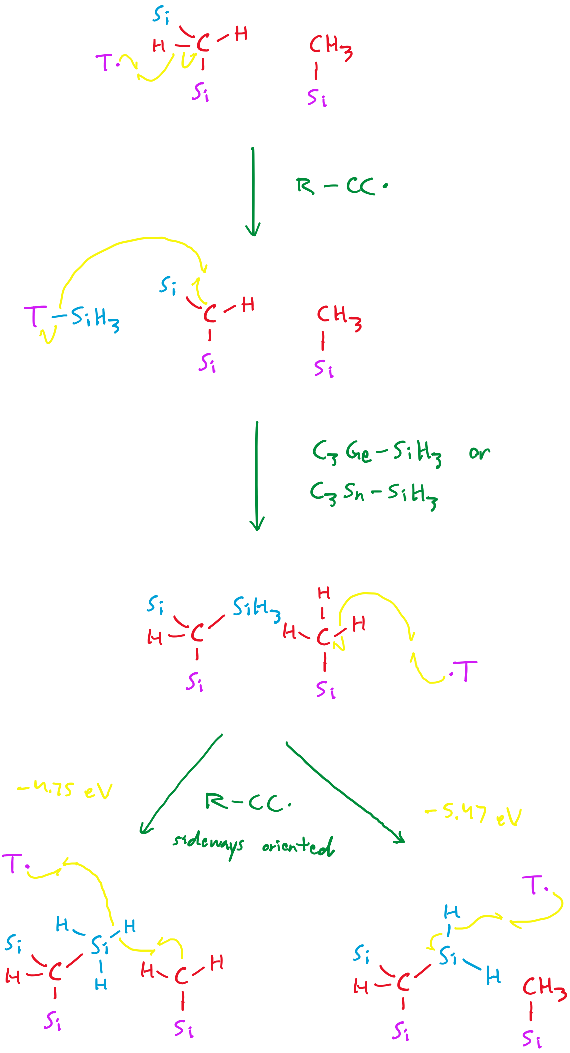
possible quantum tunneling

7)

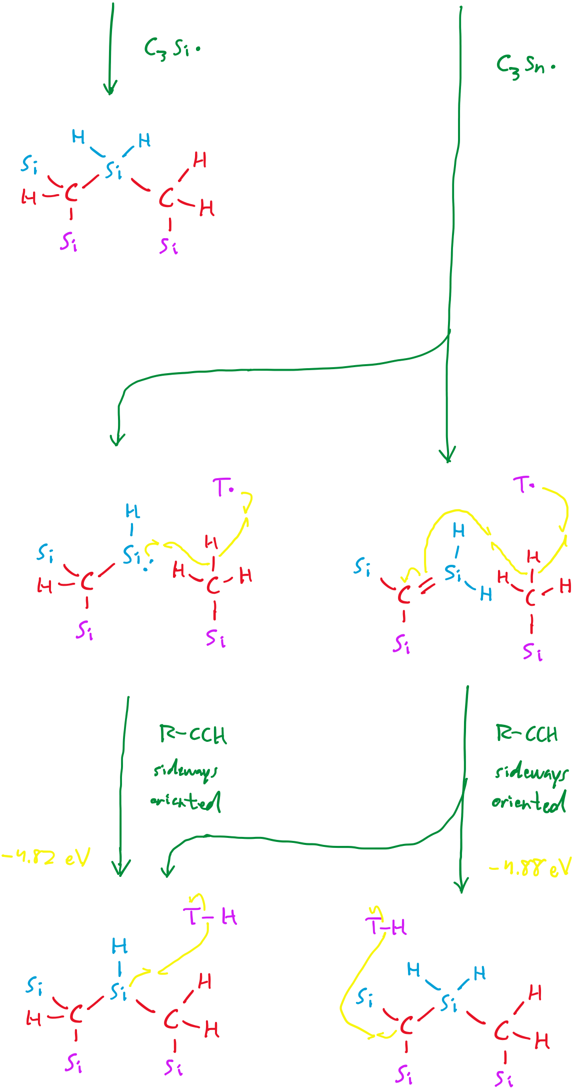

H
H
Si
Si
C
C
H
Si
Si

Graph of Outcomes Dependent on H Tunneling

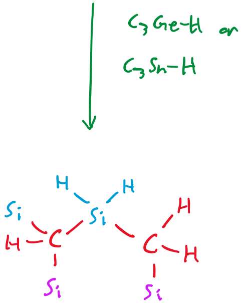
list the tooltip required for each step

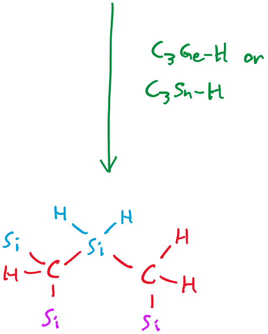


R–CC·
C₃Ge–SiH₃ or
C₃Sn–SiH₃
R–CC·
sideways oriented
-4.75 eV
-5.47 eV
T·
T–SiH₃
·T
Si
H
C
CH₃
SiH₃



C₃Si•
C₃Sn•
T•
T•
R−CCH
sideways
oriented
R−CCH
sideways
oriented
−4.82 eV
−4.88 eV
T−H
T−H

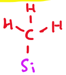
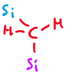
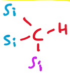
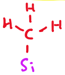
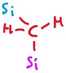
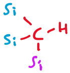

C_3Ge-H or
C_3Sn-H


C_3Ge-H or
C_3Sn-H

Variations of Lattice Extension Sequence

right side

left side

			
	1		
	2	4	
	3	5	6

assuming no additional steric congestion from atoms not described in the reaction tree above

R-CCH sideways oriented

to prevent HAbst tool from contacting Si group when removing H from C

quantum tunneling possibilities

if tunneling does happen, the rearranged product must be significantly lower in energy, or a tooltip trajectory must exist that produces the same outcome no matter which isomer is present & with flexibility of repetition / waiting

Permutations of 6-Ring Formation

1) layer initiation sequence

2) reaction tree above

3) reaction tree above, modified
    - addition of SiH_3 requires $C_3Sn\cdot$ tool
    - pathology with $C=Si$ cannot occur

4) reaction tree above, modified
    - right side positionally contrained when abstracting first hydrogen from it
    - change in energetics motivating first

H-tunneling pathology

Si_3C-SiH_3	−4.75 eV
C_3Si-CH_3	−5.47 eV
C_3Si-CH_2Si	−4.88 eV
$C_3Si-CHSi_2$	−4.61 eV

- assume 1st H tunneling flips rapidly at room temperature, instead of settling into CH_3 reliably

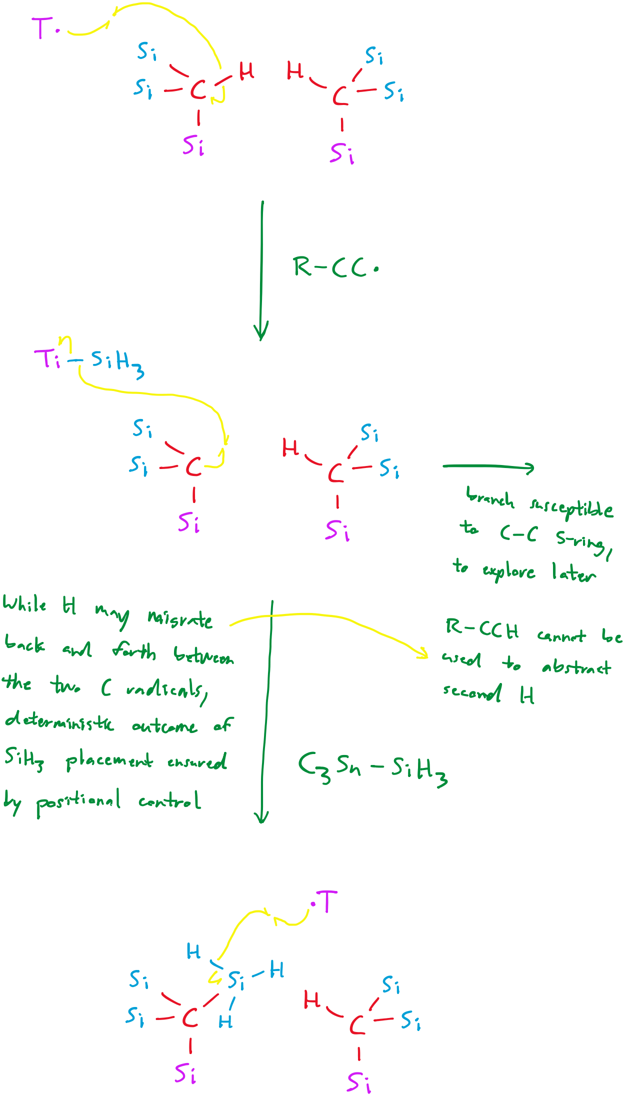
- assume that repeated application of $C_3Sn\cdot$ tool guarantees the long branch (if tunneling happens at all IRL)

- second H abstraction from C on right side is positionally constrained

5) combined changes from (3) and (4)

6) cannot abstract H from right side due to steric crowding

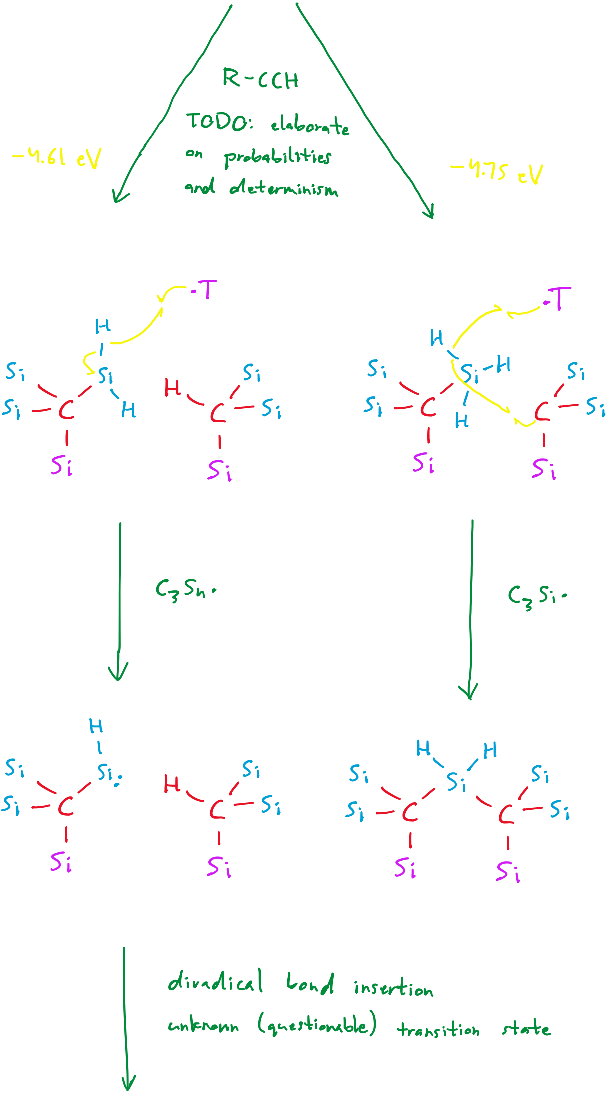
Graph of Outcomes for Case (6)


T•
Si
Si
C
H
Si
H
C
Si
Si
Si
R–CC•
Ti–SiH_3
Si
Si
C
Si
H
C
Si
Si
Si
$C_3Sn-SiH_3$
•T
H
Si
Si
Si
H
C
H
Si
H
C
Si
Si
Si

branch susceptible to C–C 5-ring, to explore later

While H may migrate back and forth between the two C radicals, deterministic outcome of SiH_3 placement ensured by positional control

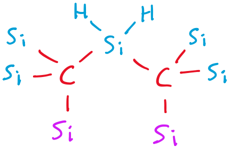
R–CCH cannot be used to abstract second H


R-CCH
-4.61 eV
-4.75 eV
·T
·T
C₃Sn·
C₃Si·

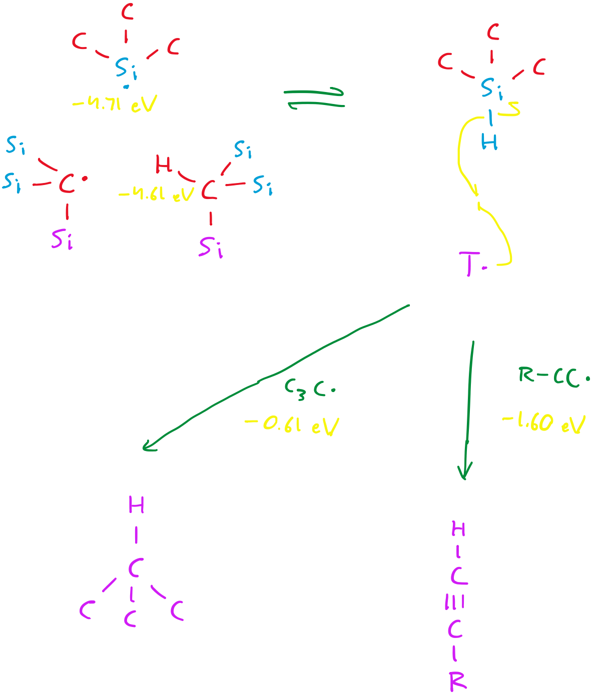
TODO: elaborate on probabilities and determinism

diradical bond insertion

unknown (questionable) transition state


H
H
Si
Si
Si
C
C
Si
Si
Si
Si

Pathway Susceptible to S-Ring Formation


C
C
C
Si
-4.71 eV
Si
Si
C
Si
H
Si
-4.61 eV
C
Si
Si
C
C
C
Si
H
T•
$C_3C•$
-0.61 eV
R-CC•
-1.60 eV
H
C
C
C
C
H
C
C
R

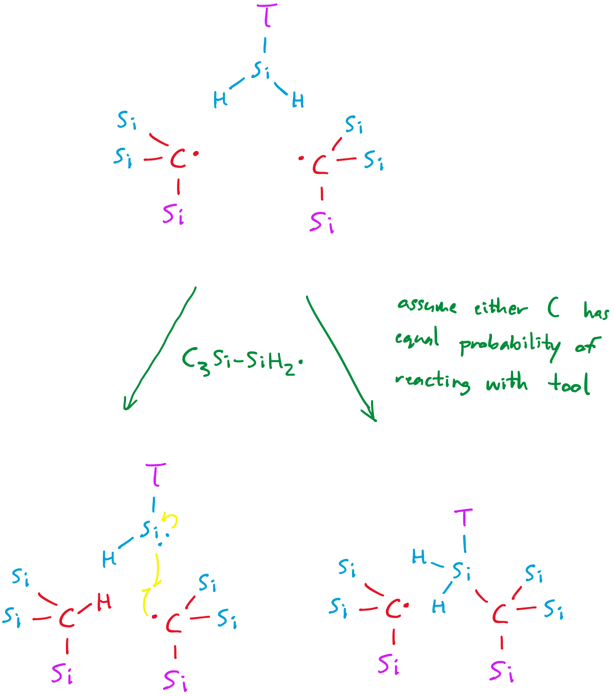
further HAbst tool recharge steps

further HAbst tool recharge steps

...

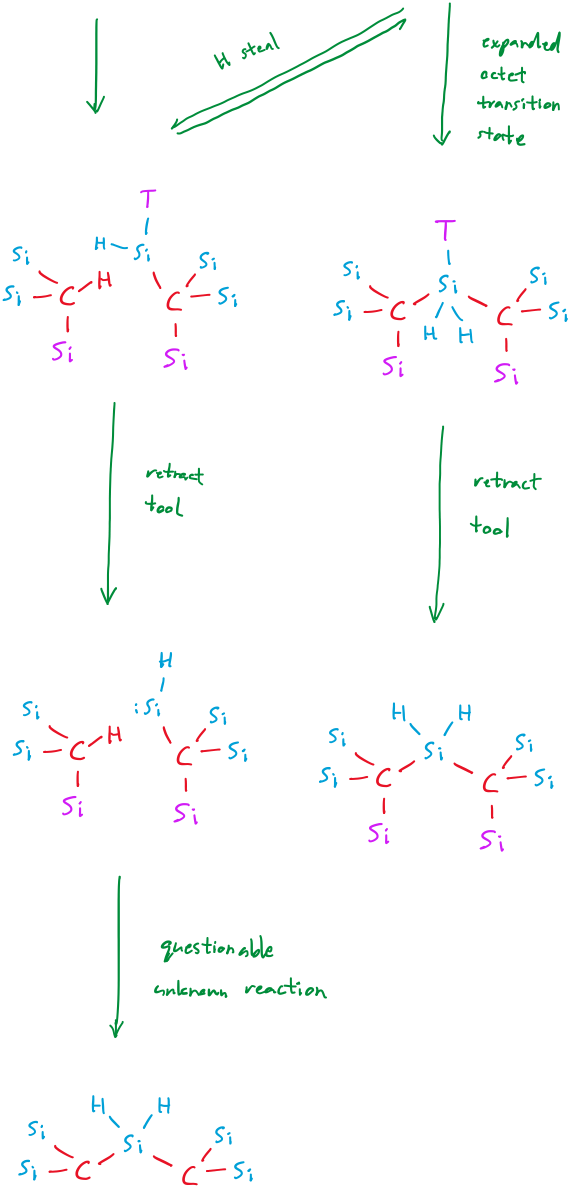
...

no data on whether the radicals will merge



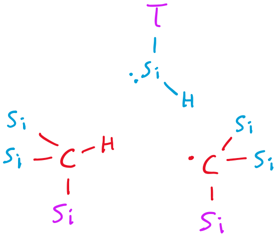
$C_3Si-SiH_2\cdot$

assume either C has equal probability of reacting with tool


H steal
expanded octet transition state
T
H
Si
C
retract tool
retract tool
questionable unknown reaction

Diradical Feedstock Pathways

first situation: not susceptible to C-C 5-ring


T
Si
H
Si
Si
C
H
Si
Si
C
Si
Si

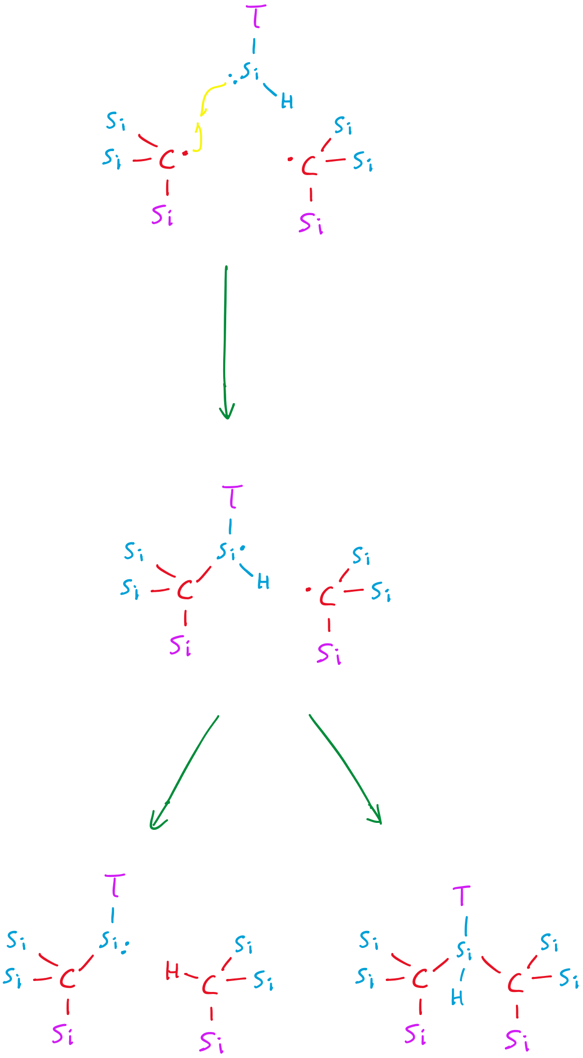
fits into the reaction tree immediately above this

second situation: susceptible to C-C 5-ring

if 5-ring forms, two possibilities:

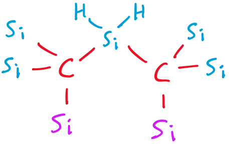
- successfully insert into strained C-C bond
- high force causes SiH: to insert into tool

better odds of using more inert feedstock to pry apart the bond by pressing against nearby Si atoms

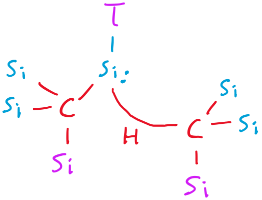

T
Si
H
Si
Si
C
Si
Si
C
Si
Si
T
Si
H
Si
Si
C
Si
Si
C
Si
Si
T
Si
Si
Si
C
Si
H
C
Si
Si
Si
T
Si
H
Si
Si
C
Si
Si
C
Si
Si

cannot immediately retract tool (equal sticking probability)

tool retraction
H donation

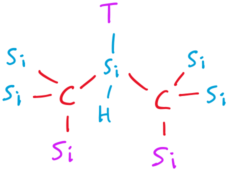


H
H
Si
Si
Si
C
Si
C
Si
Si
Si
Si



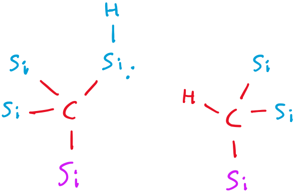
T
Si
Si
Si
C
H
C
Si
Si
Si
Si

transition state
H partially dislocated
questionable kinetics



T
Si
Si
Si
C
Si
H
C
Si
Si
Si
Si

Diradical Situation that Appears Many Times



H
Si
Si
Si
C
Si
Si
H
C
Si
Si
Si

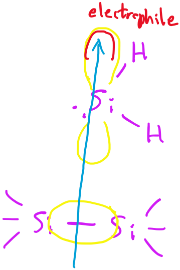
diradical will bond with $Si_3Si\cdot$

diradical will break into $Si-Si$ from the side

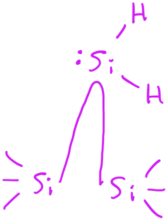
diradical will insert into C_3Sn or C_3Ge

feedstock holder with enough activation energy

$Si-H$ bond is basic and interacts w/ Lewis acids

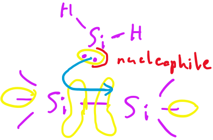

electrophile
H
Si
H
Si
Si

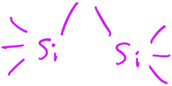
electrons filling orbital



three-center bond

electron density shift via asymmetric transition state

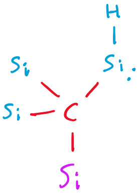

H
Si
H
nucleophile
Si
Si

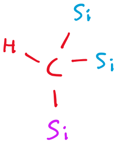


Two Most Promising Pathways Require Si: Insertion

not vulnerable to C–C 5-rings

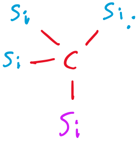
may be possible to bias reaction to an alternative H position, if model is right and system temperature can be tuned

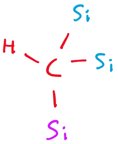

H
Si
Si
Si
C
Si



vulnerable to C–C 5-rings

tool connected to Si: provides greater chance that positional control can force a desired transition state + a different possibility for partial charge on Si atom



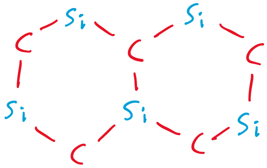


3DOF mechanosynthesis of SiC is plausible, but do not take it for granted

---

Final Attempt: Avoid the Problematic Geometry Entirely

extension of first cage


Si
Si
C
C
C
Si
Si
Si
C
C
C

can the $C=Si$ pi bond trick be used again?

$C-Si:-C$ insertion into C_3Si-H relies on same questionable logic as scenario (6) of SiC lattice extension

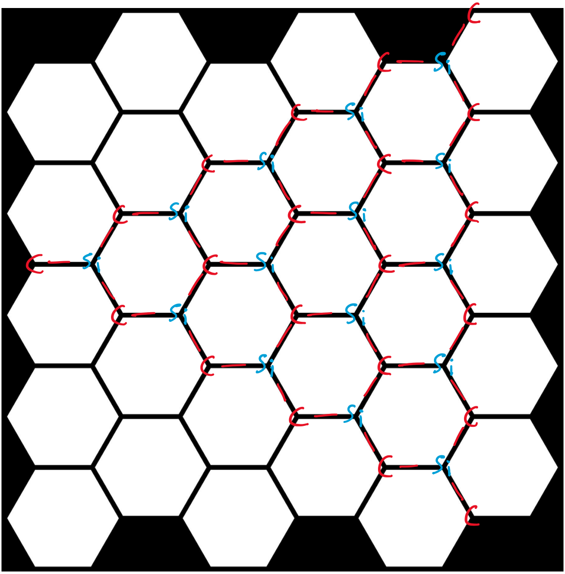
extra methyls should be inert, just like the methyl involved in ring formation

just avoid steric congestion with sideways HAbst

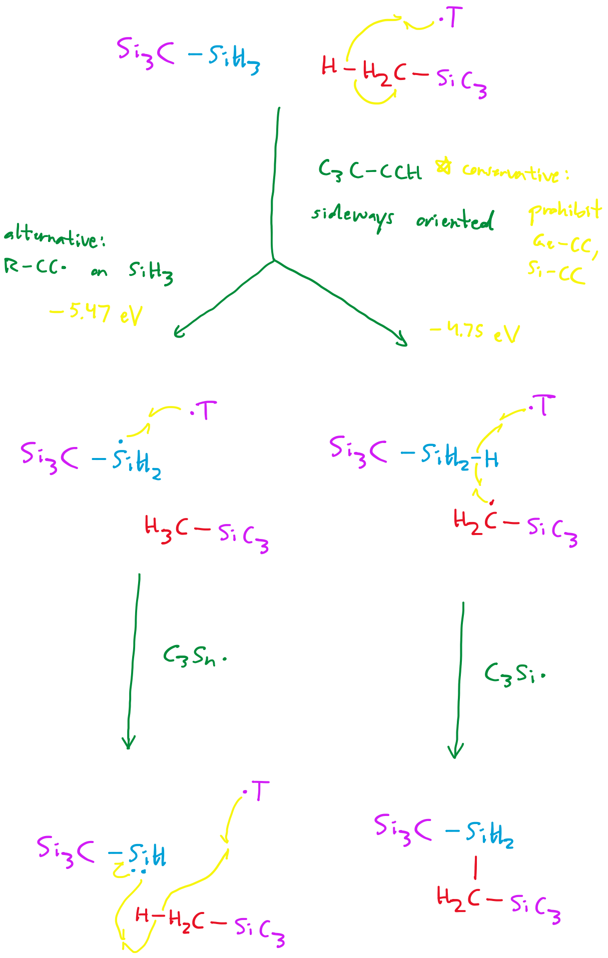
(should be guaranteed by the geometry, but conservative to impose a precautionary constraint)

careful sequence of methyl placements preceding each ring closure

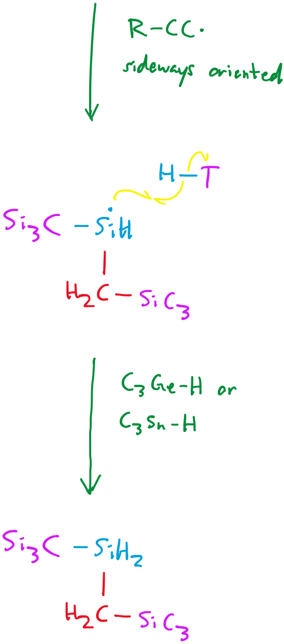
What situations would lead to case (6)?


C
Si
Si
C
C
C
Si
Si
C
C
Si
Si
C
C
Si
Si
Si
C
C
C
Si
Si
Si
C
C
C
Si
Si
C
C
Si
Si
C
C
Si
C

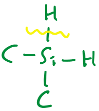
alternative to concerted mechanism for finishing 6-ring when C group is strong, and if H tunneling does happen IRL this should apply to cases (2), (3), (4), (5) as long as C can be attacked from back side



Si_3C-SiH_3
·T
$H-H_2C-SiC_3$
C_3C-CCH ☆ conservative:
sideways oriented
prohibit Ge−CC, Si−CC
alternative:
R−CC· on SiH_3
−5.47 eV
−4.75 eV
·T
$Si_3C-\dot{S}iH_2$
H_3C-SiC_3
·T
Si_3C-SiH_2-H
$H_2\dot{C}-SiC_3$
C_3Sn·
C_3Si·
·T
Si_3C-SiH
$H-H_2C-SiC_3$
Si_3C-SiH_2
H_2C-SiC_3


R–CC·
sideways oriented
H–T
Si3C –SiH
H2C – SiC3
C3Ge–H or
C3Sn–H
Si3C –SiH2
H2C – SiC3

possible tools

	4.82 eV
C_3Si-H	4.72 eV
C_3Ge-H	4.01 eV
C_3Sn-H	3.29 eV

Issue with Si on Edge of Lattice

MinToolset paper turns Ge into a full diradical before adding methylene to it, possibly to eliminate issues with carbene pathology

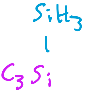
safe to assume 4-ring unlikely to occur between C· and Si: due to immense energetic barrier from strain, but 5-ring pathologies likely will occur

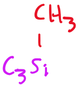
with SiC build plate instead of Si build plate, we can afford less questionable lattice initiation that doesn't have $CH_2\cdot$ + $SiH_2\cdot$ reaction or require SiH: feedstock

may remove need for troublesome $SiH_2\cdot$ feedstock too and no need for direct CH_3 donation (not simulated)

$C_3Sn-SiH_3$

$C_3Ge-CH_2\cdot$ or
$C_3Sn-CH_2\cdot$


$C_3Si-SiH_3$


C_3Si-CH_3

$C_3Si-SiH_3$ −3.10 eV
$C_3Ge-SiH_3$ −2.96 eV
$C_3Sn-SiH_3$ −2.34 eV
$HC_2Si-SiH_3$ −3.07 eV to −3.19 eV

$C_3Si-CH_2\cdot$ −4.38 eV
$C_3Ge-CH_2\cdot$ −3.71 eV
$C_3Sn-CH_2\cdot$ −2.61 eV
$\underline{HC_2Si-CH_2\cdot}$ −4.45 eV

WARNING: bad reaction

new layer initiation:

place methyls

HAbst (R-CC·)

CH_2 ($C_3Ge{-}CH_2\cdot$ or $C_3Sn{-}H$)

H ($C_3Ge{-}H$)

place silyl

HAbst ($R{-}CC\cdot$)

SiH_3 ($C_3Sn{-}SiH_3$)

reduce Si group to diradical ← avoids the need to worry about alternative paths

$C_3Si{-}SiH_3 \longrightarrow C_3Si{-}SiH_2\cdot$

−4.58 eV

use $R{-}CC\cdot$ tool

$C_3Si{-}SiH_2\cdot \longrightarrow C_3Si{-}SiH{:}$

$C_3Si{-}\overset{\cdot}{Si}H \wr H$ −3.18 eV / −3.40 eV

$Si_3C{-}\overset{\cdot}{Si}H \wr H$ −3.11 eV

$C_3Ge \wr H$ −3.86 eV / −4.11 eV / −4.01 eV

$C_3Sn \wr H$ −3.29 eV

$HC_2Si \wr \overset{\cdot}{Si}H_2$ −2.09 eV / −1.98 eV

$C_3Si \wr \overset{\cdot}{Si}H_2$ −2.02 eV / −1.94 eV / −1.99 eV

$Si_3C \wr \overset{\cdot}{Si}H_2$ −1.76 eV

$C_3Ge \wr \overset{\cdot}{Si}H_2$ −1.80 eV / −1.82 eV / −1.84 eV

$C_3Sn \wr \overset{\cdot}{Si}H_2$ −1.42 eV

$HC_2Si \wr SiH_3$ −3.19 eV / −3.07 eV

$C_3Si{\wr}SiH_3$ -3.14 eV / -3.01 eV / -3.10 eV

$Si_3C{\wr}SiH_3$ -3.06 eV

$C_3Ge{\wr}SiH_3$ -2.95 eV / -2.93 eV / -2.96 eV

$C_3Sn{\wr}SiH_3$ -2.34 eV

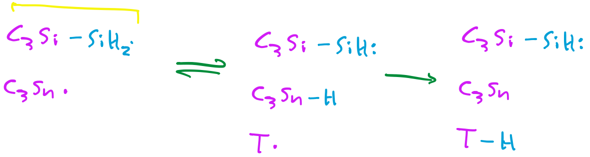
energies for SiH_3 are to corroborate trends with energies for $SiH_2\cdot$

also check "DiradicalFeedstocks" for reference

$C_3Sn\cdot$ is okay for H abstraction, as long as multiple attempts are used

multiple attempts OK because all reactions involved are reversible

substituting $Si_3C{-}SiH_2\cdot$ works as well


$C_3Si-SiH_2\cdot$
$C_3Sn\cdot$
$C_3Si-SiH:$
C_3Sn-H
$T\cdot$
$C_3Si-SiH:$
C_3Sn
$T-H$

requirement: C_3Sn-T complex can be easily broken

$C_3Ge\cdot$ or $C_3Si\cdot$ qualifies as tool

new layer initiation sequence:

place methyls

place silyl

turn silyl into $SiH:$

turn methyl into $CH_2\cdot$

form 5-ring with $Si-\dot{Si}H-C$

passivate Si radical

either C_3Ge-H or C_3Sn-H qualifies

use similar idea for second Si–C bond

form $Si-\ddot{Si}-C$

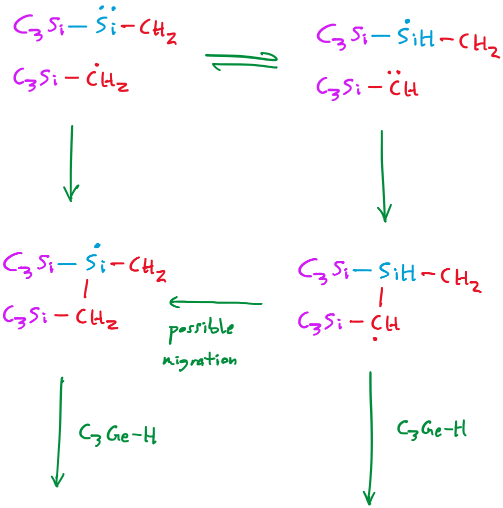
form $CH_2\cdot$

nudge together with either thermal energy

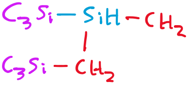
or force from inert tooltip

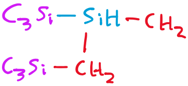
$(Si: + CH_3 \longrightarrow SiH_2\cdot + CH_2\cdot$ very unlikely$)$

carbene pathology:



$C_3Si-\ddot{Si}-CH_2$
$C_3Si-\dot{C}H_2$
$C_3Si-\dot{Si}H-CH_2$
$C_3Si-\ddot{C}H$
$C_3Si-\dot{Si}-CH_2$
C_3Si-CH_2
$C_3Si-SiH-CH_2$
$C_3Si-\dot{C}H$
possible migration
C_3Ge-H
C_3Ge-H


C3Si
SiH
CH2
C3Si
CH2


C3Si
SiH
CH2
C3Si
CH2

safe; just apply HDon tool repeatedly

Si=C pi bond trick still used to complete cage

use carbene protection trick to close 6-rings during lattice extension

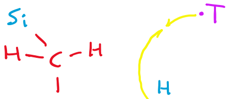
Reaction Tree at Edge of Crystal

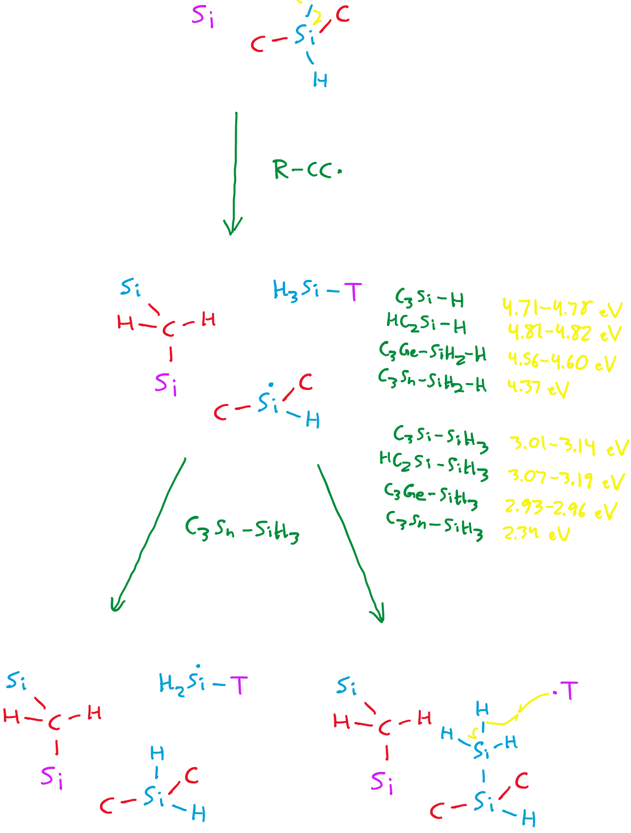
two cases:

- apply SiH_3 to silicon radical
- apply SiH_3 to carbon radical

investigate tomorrow

First case: apply SiH_3 to silicon radical, assuming CH_3 won't deposit in an S_N2 mechanism and that H-passivation is mandatory for all atoms on the edge




Si
C–Si–C
H
R–CC•
Si
H–C–H
Si
H3Si–T
C–Si•–C
H
C3Sn–SiH3
Si
H–C–H
Si
H2Si•–T
H
C–Si–C
H
Si
H–C–H
Si
H
H–Si–H
•T
C–Si–C
H

C_3Si-H	4.71–4.78 eV
HC_2Si-H	4.81–4.82 eV
$C_3Ge-SiH_2-H$	4.56–4.60 eV
$C_3Sn-SiH_2-H$	4.37 eV
$C_3Si-SiH_3$	3.01–3.14 eV
$HC_2Si-SiH_3$	3.07–3.19 eV
$C_3Ge-SiH_3$	2.93–2.96 eV
$C_3Sn-SiH_3$	2.34 eV

H transfer energetics:

4.37 eV → 4.75 eV

4.37 eV → 4.82 eV

C_3Si site −0.38 eV

HC_2Si site −0.45 eV

SiH_3 transfer energetics

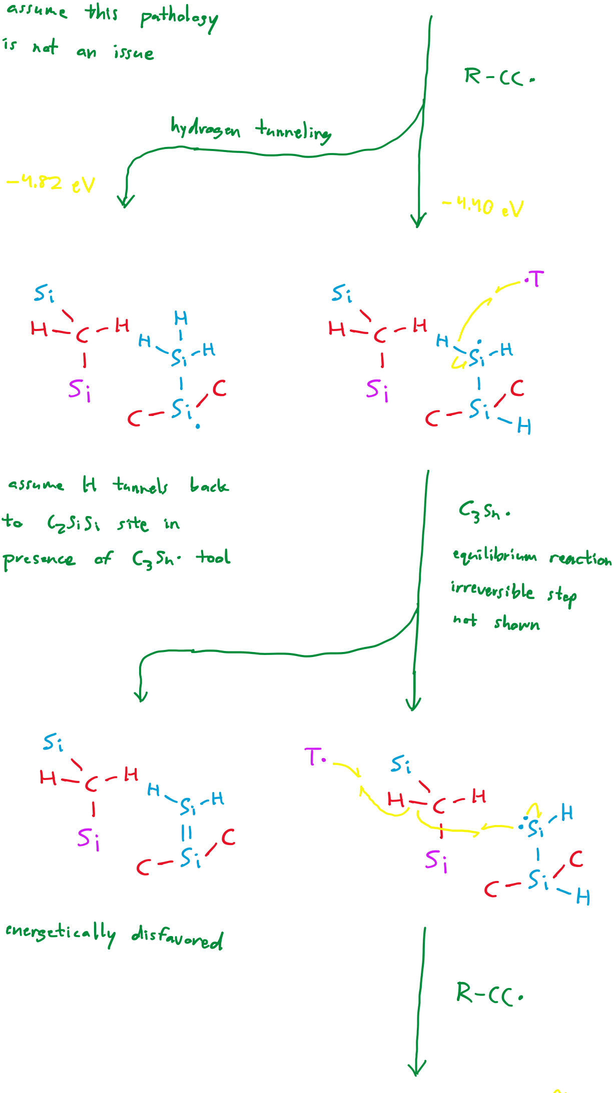
2.34 eV → 3.08 eV

2.34 eV → 3.13 eV

C_3Si site −0.74 eV

HC_2Si site −0.79 eV

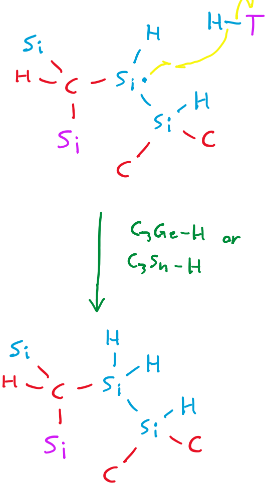
assume this pathology is not an issue


R-CC·
hydrogen tunneling
-4.82 eV
-4.40 eV
Si
H
C
Si
·T
T·
C3Sn·
R-CC·

assume H tunnels back to C_2SiSi site in presence of $C_3Sn\cdot$ tool

$C_3Sn\cdot$ equilibrium reaction irreversible step not shown

energetically disfavored


H–T
Si
H
C
Si
Si
H
C
C
C_3Ge–H or
C_3Sn–H

following steps:

turn Si into diradical

turn next C into radical

induce C-Si bond formation

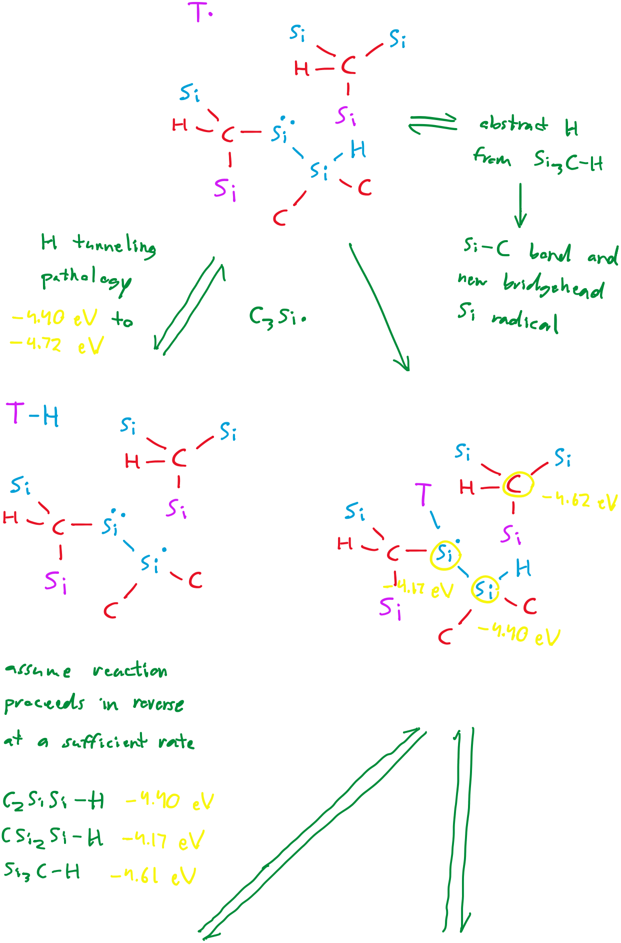
C=Si pi bond trick

hydrogenate Si bridgehead

pathology: H migrates from underside Si to top Si, then to $CH_2\cdot$ before creating pi bond

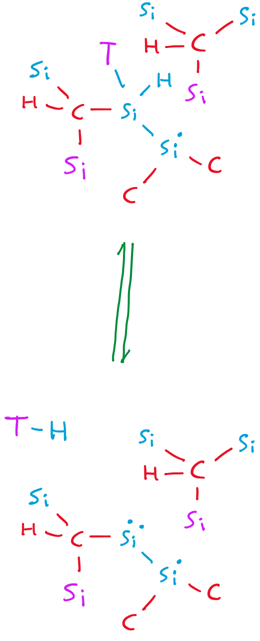
assume pathology is not an issue

topological issue when 2nd C is in Si_3C/Si_3C–H


T·
Si
Si
H
C
Si
H
C
Si
Si
Si
H
Si
C
C
abstract H from Si_3C-H
Si–C bond and new bridgehead Si radical
H tunneling pathology
−4.40 eV to −4.72 eV
$C_3Si\cdot$
T-H
T
−4.62 eV
−4.17 eV
−4.40 eV

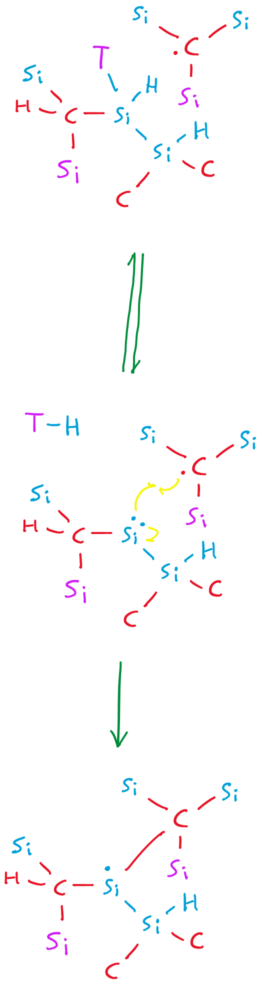
assume reaction proceeds in reverse at a sufficient rate

$C_2SiSi-H$ −4.40 eV
CSi_2Si-H −4.17 eV
Si_3C-H −4.61 eV



possible unexpected good outcome:

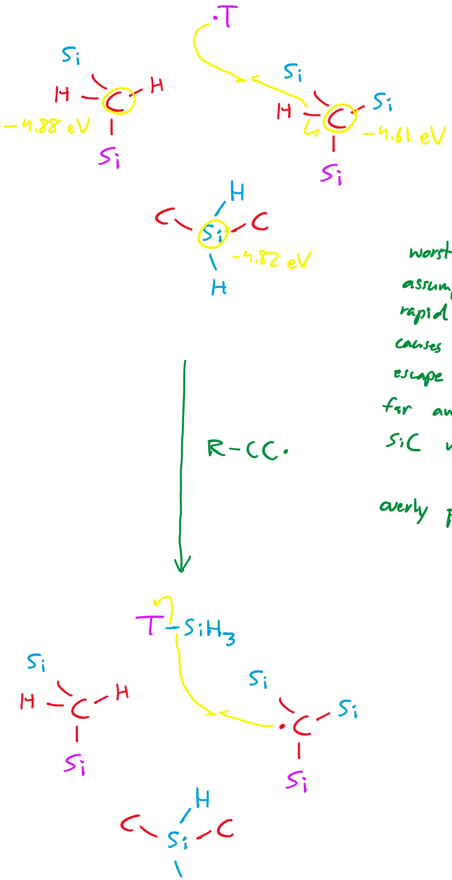
H tunnels from $Si_3C \longrightarrow C_2SiSi$ in equilibrium, permitting irreversible radical-radical coupling between Si: and C·



H may migrate between the two C_2SiSi sites in equilibrium, but approach of C_3Ge-H or C_3Sn-H

guarantees full passivation

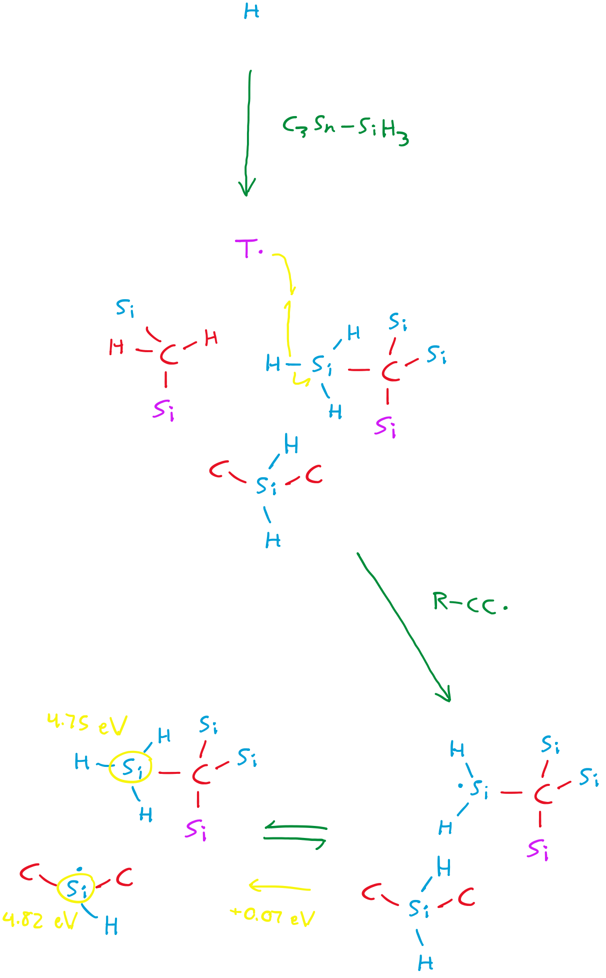
second case: apply SiH_3 to C radical



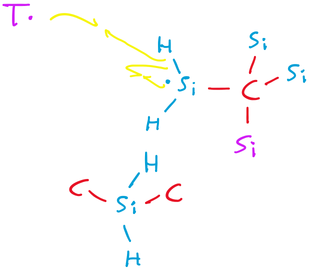
·T
Si
H
C
H
Si
−4.88 eV
Si
H
C
Si
Si
−4.61 eV
H
C
Si
C
H
−4.82 eV
R−CC·
T−SiH₃
Si
H
C
H
Si
Si
·C
Si
Si
H
C
Si
C

worst case
assumption:
rapid tunneling,
causes H to
escape to somewhere
far away on the
SiC workpiece

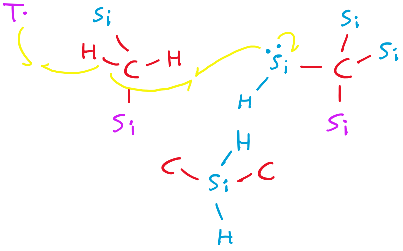
overly pessimistic


H
C3Sn–SiH3
T·
R–CC·
4.75 eV
4.82 eV
+0.07 eV

if H tunneling does occur, assume reverse pathway happens quickly break in the reaction tree for clarity


T·
H
Si
Si
C
Si
H
Si
H
C
Si
C
H

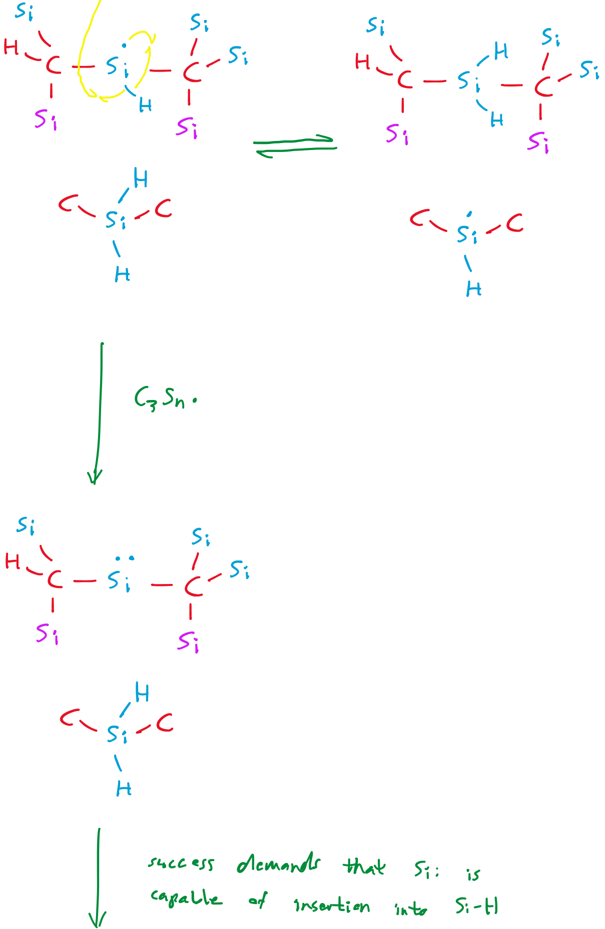
$C_3Sn\cdot$ (equilibrium) followed by repeated applications of $C_3Sn\cdot \rightarrow C_3Si\cdot / C_3Ge\cdot$ (irreversible)


T·
Si
H
C
H
Si
Si
Si
C
Si
H
Si
H
C
Si
C
H

TODO: explore branch where SiH: prefers to insert into other Si–H bond

R–CC·

depends on whether H tunneling occurs at all; assume reversible

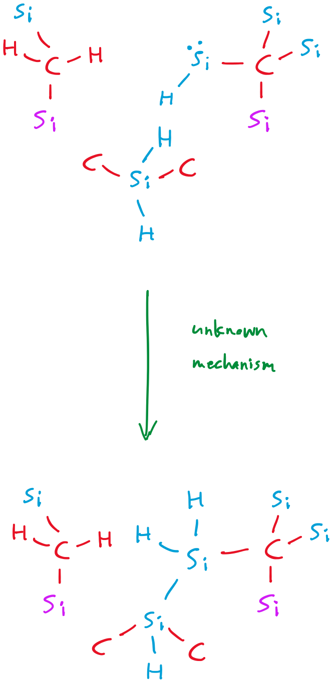


success demands that Si: is capable of insertion into Si-H
more plausible than previous issue with C-H insertion for case (6)

Branch with Early Si-H Insertion

if this happens at all IRL, assume it can

be made to happen 100% of the time
by waiting long enough


unknown
mechanism

following steps:

form Si diradical

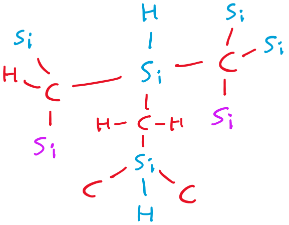
form C radical

induce C–Si bond formation

use C = Si pi bond trick

assume the pathologies are okay

hydrogenate the Si bridgehead with Ge-H or Sn-H


H
Si
Si
Si
H
C
Si
C
H
C
H
Si
Si
Si
C
C
H

Summary of the New Primitive

forms new cage on edge of lattice

requires two nearby $Si-CH_2-Si$, up to one of which may be $Si-CHSi_2$

Option 1

relies on H tunneling at crowded site or absence of bond formation between $C_2Si:$ and $C_3Si\cdot$

abstract H from C_2SiH_2

donate SiH_3 to $C_2\dot{S}iH$

turn SiH_3 into diradical

turn CH into radical

induce Si–C bond formation

turn CSiSi into diradical

(1) second carbon is $Si-CH_2-Si$

form radical by sideways approach of HAbst

(2) second carbon is $Si-CHSi_2$

turn $CHSi_2$ into radical

$C_3Si\cdot$ tool employed

relies on equilibriation of H tunneling

irreversible step of equilibriation forms C–Si bond

second C–Si bond forms

deposit CH_2 onto Si radical with $Ge{-}CH_2\cdot$

rely on thermal motion to break C=Si pi bond

donate H with Ge–H or Sn–H

Option 2 relies on Si: insertion into $C_2HSi{-}H$

(1) second carbon is $Si{-}CH_2{-}Si$

abstract H from C with R–CC·

deposit SiH_3 with $C_3Sn{-}SiH_3$

slightly more susceptible to H steal, but the steal might be reversible

(2) second carbon is $Si{-}CHSi_2$

abstract H from C with R–CC·

deposit SiH_3 with $C_3Sn{-}SiH_3$

turn SiH_3 into diradical

(1) insertion into $C_2HSi{-}H$ happens immediately

turn $CSiSiH_2$ into diradical 2 HAbst 1 HAbst

turn first carbon into radical (sideways R–CC·)

induce C–Si bond formation

(2) insertion into $C_2HSi{-}H$ happens later

turn first carbon into radical (sideways R–CC·)
↑ 1 HAbst
turn C_2SiH into diradical 1 HAbst
induce C_2Si: insertion into Si–H bond
abstract H from bridgehead Si

deposit CH_2 onto Si radical with Ge–CH_2·
rely on thermal motion to break C=Si pi bond
donate H with Ge–H or Sn–H

Summary of Verified Primitives

all primitives spawn a new cage from scratch

(1) layer initiation
requires 4 C_3Si–H sites
- ☐ reliance on Si: insertion into Si–H
- ☐ reliance on H tunneling
- ☐ use of SiH_2· feedstock
- ☐ reliance on sideways HAbst
- ☑ reliance on thermal or forced activation of barrier

(2) lattice extension

third case
$CH_3 + CH_2$

requires 1 C_3Si–CH_3 site nearby
requires either Si–CH_2–Si + Si–CH_2–Si
or Si–CH_2–Si + Si–CH–Si_2
- ☐ reliance on Si: insertion into Si–H
- ☐ reliance on H tunneling

☐ use of $SiH_2\cdot$ feedstock
☑ reliance on sideways HAbst
☐ reliance on thermal or forced activation of barrier

(3) edge completion 1

requires 1 $HC_2Si{-}H$ site nearby

requires either $Si{-}CH_2{-}Si$ + $Si{-}CH_2{-}Si$

or $Si{-}CH_2{-}Si$ + $Si{-}CH{-}Si_2$

☐ reliance on Si: insertion into Si–H
☑ reliance on H tunneling
☐ use of $SiH_2\cdot$ feedstock
☐ reliance on sideways HAbst
☑ reliance on thermal or forced activation of barrier

(4) edge completion 2

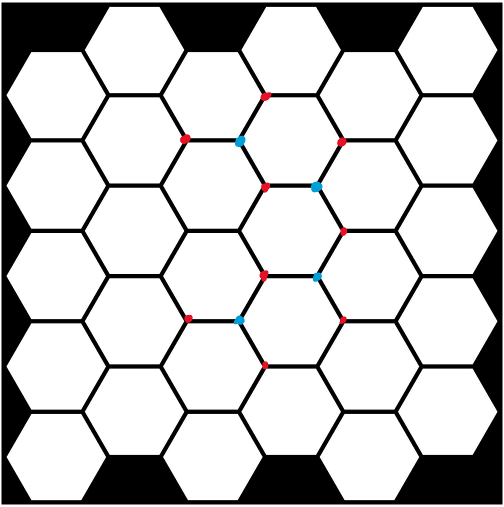
requires 1 $HC_2Si{-}H$ site nearby

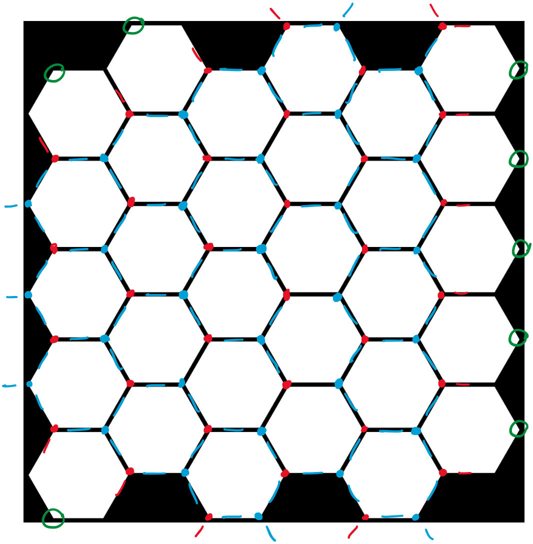
requires either $Si{-}CH_2{-}Si$ + $Si{-}CH_2{-}Si$

or $Si{-}CH_2{-}Si$ + $Si{-}CH{-}Si_2$

☑ reliance on Si: insertion into Si–H
☐ reliance on H tunneling
☐ use of $SiH_2\cdot$ feedstock
☑ reliance on sideways HAbst
☑ reliance on thermal or forced activation of barrier

case (6)





○ $HC_2Si{-}H$

• $Si{-}CH_2{-}Si$

● $Si{-}CH{-}Si_2$

try starting with primitive (1) on problematic edges

modification to primitive (1)

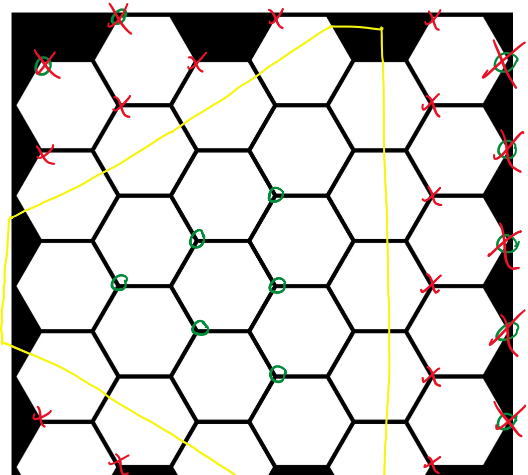
SiH_3 can be placed on $HC_2Si\cdot$

at least one CH_2 must be able to flex

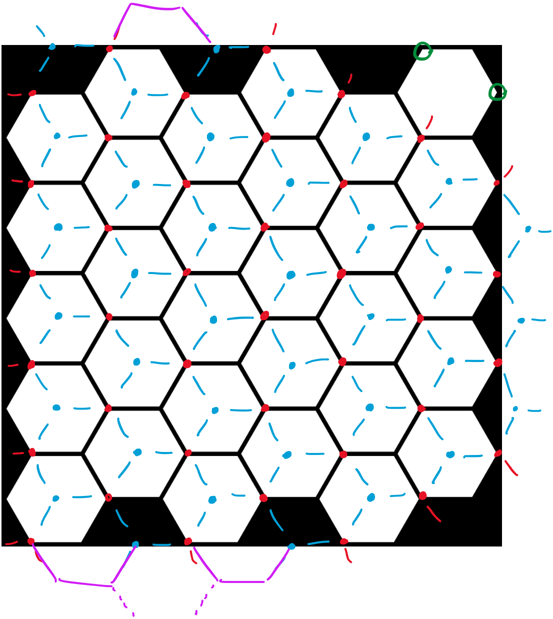
to form strained complex with 2 5-rings

doesn't fix the problem

Try Building Hexagonal Lattice that Avoids These Edges



Try Building a Cubic Lattice Instead



hexagonal: end cell would be 4-ring

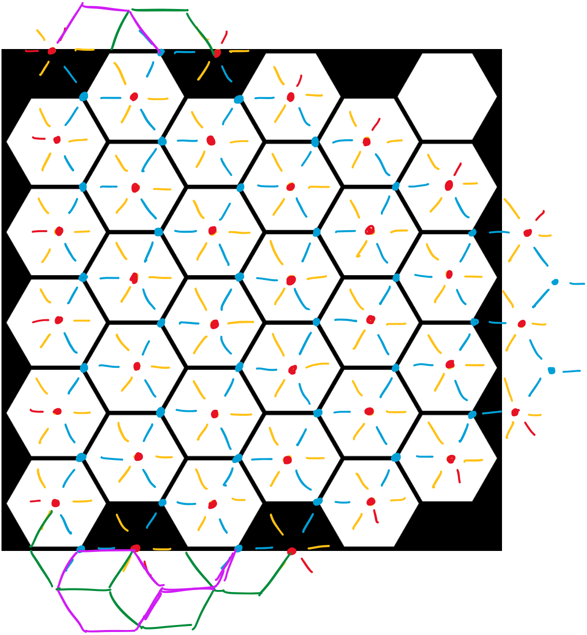
cubic: end cell completes cage

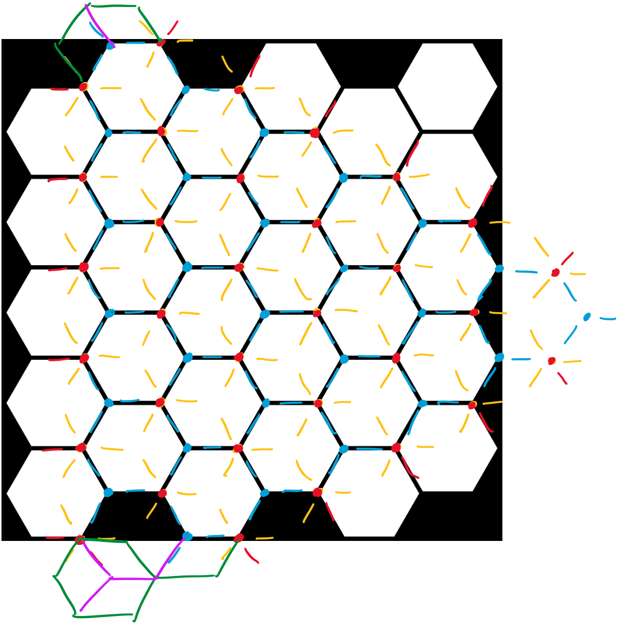
rigorously double-check cubic for topology violations, then analyze what crystal surfaces are being built

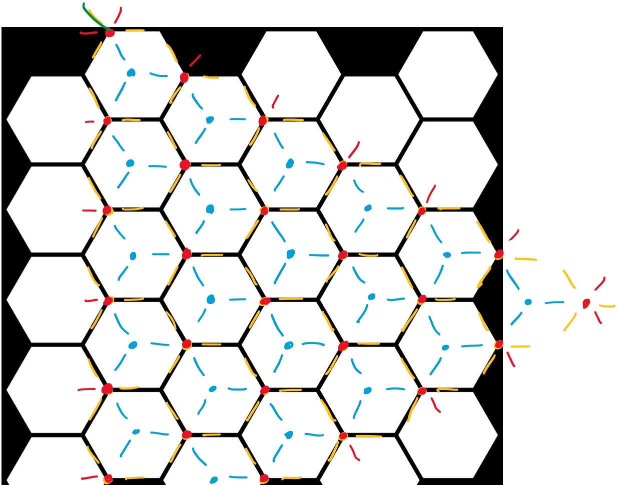
build 3 layers in succession

there might be a path for overhangs that relies on long-lived pi bonds, and using the CH_2 of the pi bond instead of sp^3 CH_2

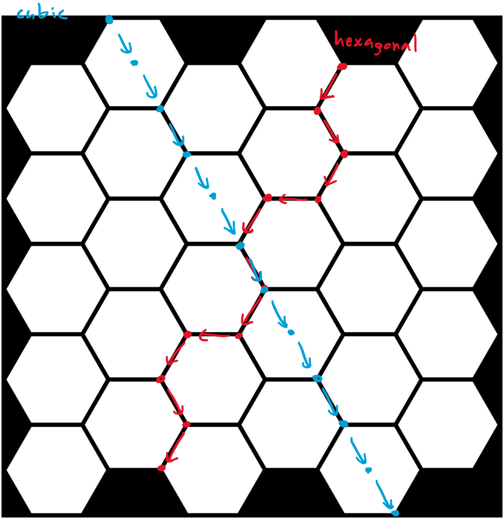
don't investigate this pathway for now







(111) edges are gradually shrinking

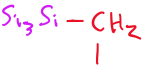

cubic
hexagonal

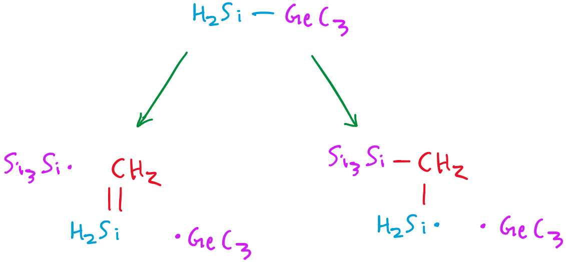
Can more overhangs fix this? NO

Need a New Primitive

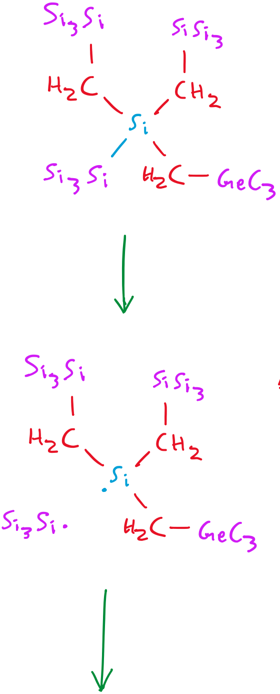
$C=Si$ pi bond trick on Si(111)

simulated reaction


Si_3Si-CH_2

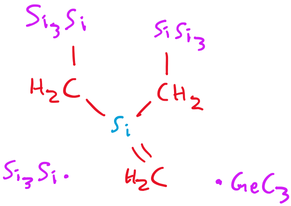

H2Si — GeC3
Si3Si•
CH2
H2Si
•GeC3
Si3Si — CH2
H2Si•
•GeC3

simulated reaction


Si3Si
SiSi3
H2C
CH2
Si
Si3Si
H2C — GeC3
Si3Si
SiSi3
H2C
CH2
•Si
Si3Si•
H2C — GeC3

⚠ Si_3Si-Si energy not the same as C_3Si-Si energy

$C_3Ge-CH_2\cdot$	−3.60 eV
C_3Ge-CH_3	−3.59 eV
$Si_3Si-SiH_2\cdot$	−1.42 eV
$Si_3Si-SiH_3$	−2.43 eV

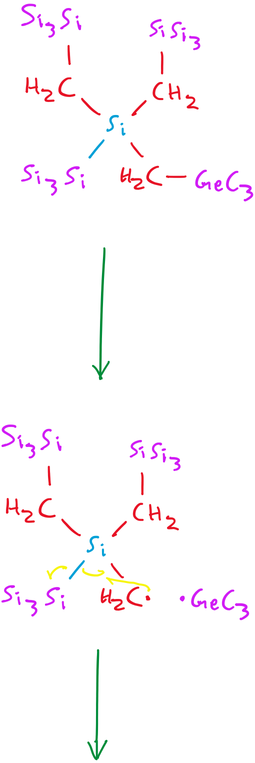


Si_3Si
$SiSi_3$
H_2C
CH_2
Si
$Si_3Si\cdot$
H_2C
$\cdot GeC_3$

$C_3Si-SiH_2\cdot$ −2.02 eV

$C_3Si-SiH_3$ −3.14 eV

alternative explanation



Si_3Si
$SiSi_3$
H_2C
CH_2
Si
Si_3Si
H_2C-GeC_3
Si_3Si
$SiSi_3$
H_2C
CH_2
Si
Si_3Si
$H_2C\cdot$
$\cdot GeC_3$

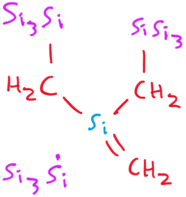
$C_3Ge-CH_2\cdot$ −3.71 eV

$C_3Si-CH_2\cdot$ −4.38 eV

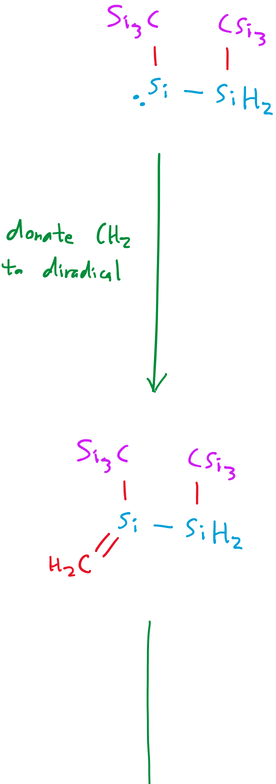
$C_2SiSi-CH_2\cdot$ −4.28 eV

$CSi_2Si-CH_2\cdot$ −4.19 eV

$Si_3Si-CH_2\cdot$ −4.01 eV



proposed reaction site


donate CH_2 to diradical

plausible to form; worry about later

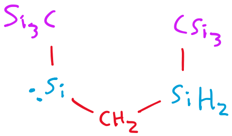
Si_3C-SiX about as strong as $C_3Si-SiX$, $C_3Ge-SiX$, but stronger than $Si_3Si-SiX$

no need for bond scission to form pi bond

Ge tool had ~equal pulling force as Si_3Si site, Si–Si bond cleavage may have been due to electronic effects instead of mechanical force

Si radical preferred over C radical

uncertain whether recoil (localized thermal energy) will overcome barrier to lower energy state

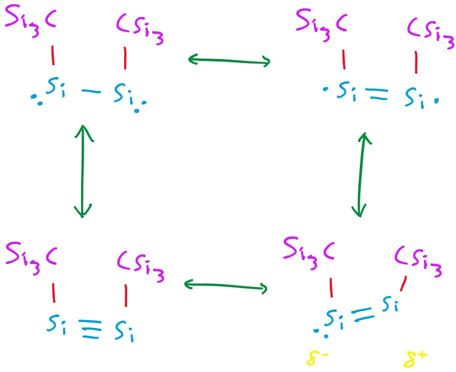

Si3C
CSi3
Si
CH2
SiH2

Alternative

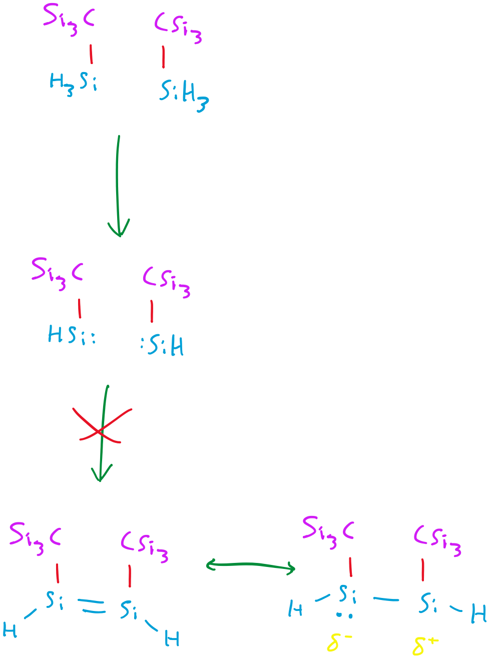
must be pair of diradicals to avoid uncertainty over position of H due to tunneling

⟶ very easy for R–CH$_2$· to steal the H

don't know whether this structure is stable in xTB


Si3C
CSi3
Si
Si
δ-
δ+

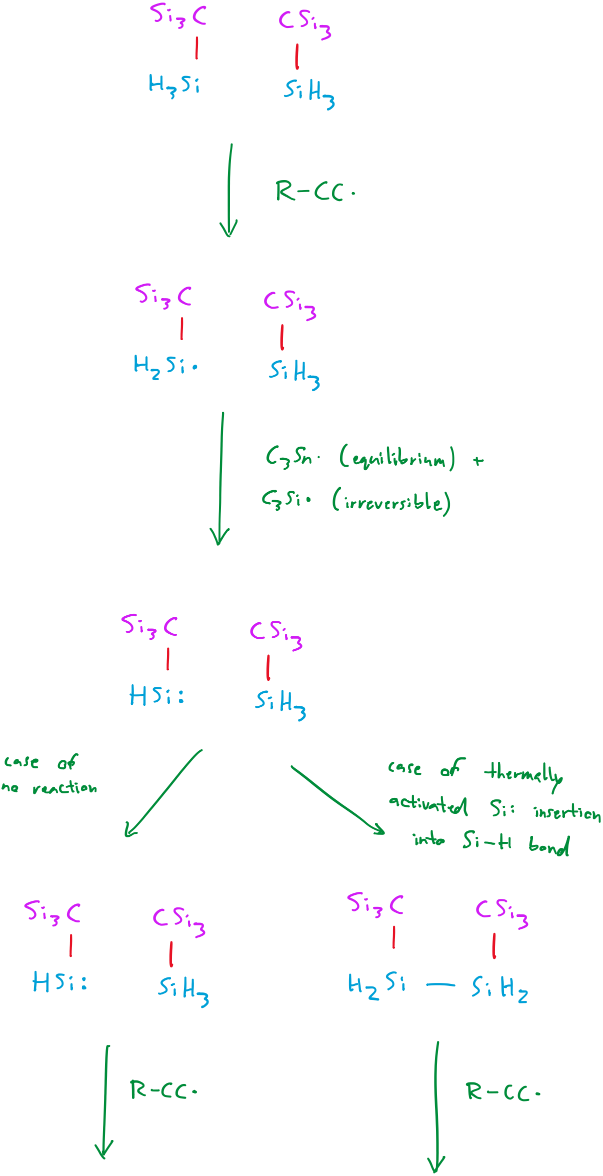
problem with formation

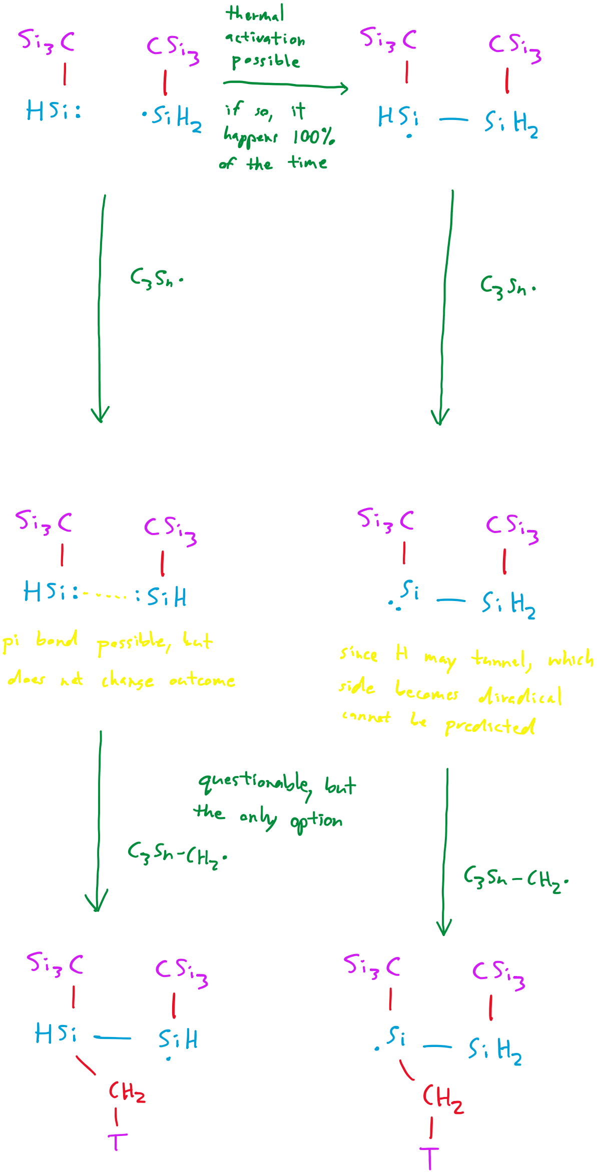


Si3C
CSi3
H3Si
SiH3
Si3C
CSi3
HSi::
:SiH
Si3C
CSi3
Si
Si
H
H
Si3C
CSi3
H
Si
Si
H
δ-
δ+

$H_2Si=SiH_2 \longrightarrow H_3Si-SiH$

both states are close in energy


Si3C
CSi3
H3Si
SiH3
R–CC·
Si3C
CSi3
H2Si·
SiH3
C3Sn· (equilibrium) +
C3Si· (irreversible)
Si3C
CSi3
HSi:
SiH3
case of no reaction
case of thermally activated Si: insertion into Si–H bond
Si3C
CSi3
HSi:
SiH3
Si3C
CSi3
H2Si — SiH2
R-CC·
R-CC·


Si3C
CSi3
HSi:
•SiH2
HSi
SiH2
C3Sn•
C3Sn•
HSi:·····:SiH
Si
C3Sn-CH2•
C3Sn-CH2•
HSi
SiH
CH2
T
Si
SiH2
CH2
T

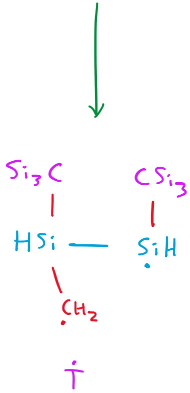
thermal activation possible

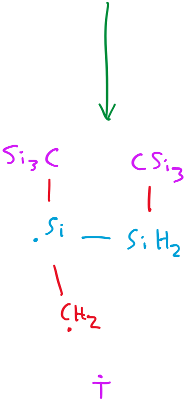
if so, it happens 100% of the time

pi bond possible, but does not change outcome

since H may tunnel, which side becomes diradical cannot be predicted

questionable, but the only option


Si3C
CSi3
HSi
SiH
CH2
T


Si3C
CSi3
Si
SiH2
CH2
T

hydrogen does not tunnel across the 2 sides of a Si(100) dimer at room temperature?

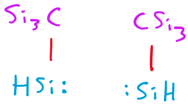
Pitters et al. (2024)

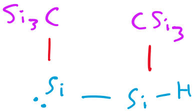
DB motion suppressed below 500 K

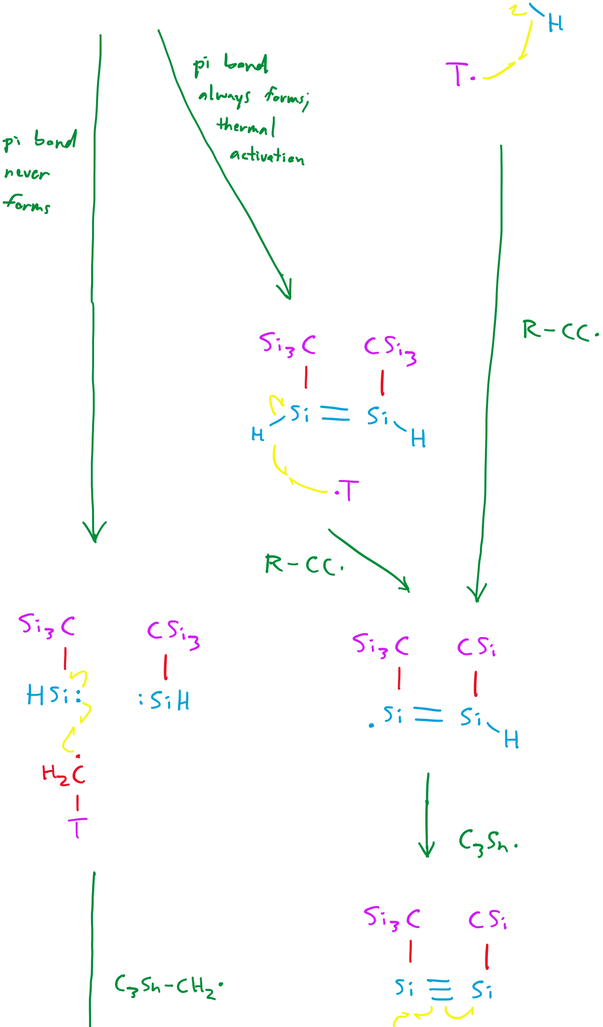
* * *

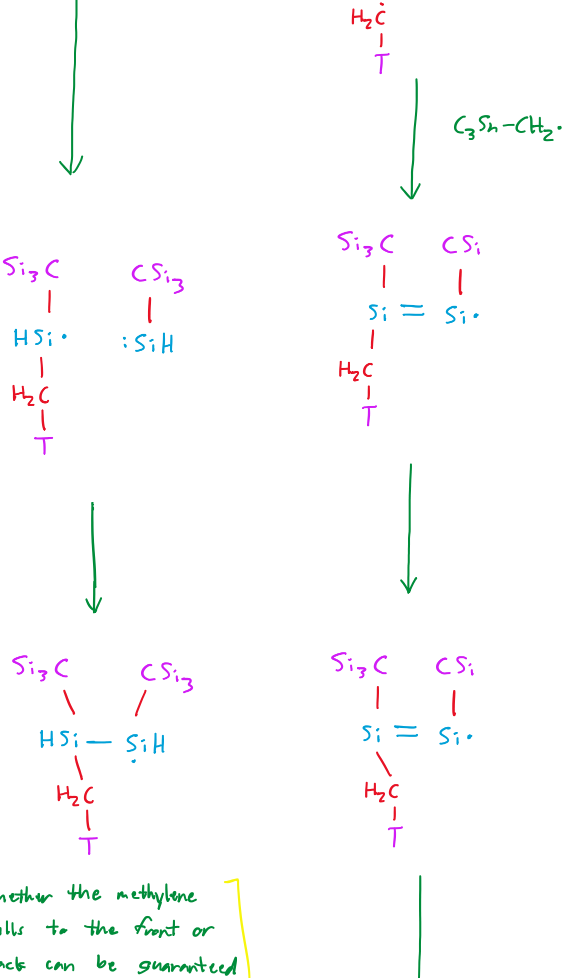
Revising the Previous Tree

exact side known, guaranteed by positional control


Si3C
CSi3
HSi:
:SiH


Si3C
CSi3
Si
Si
H

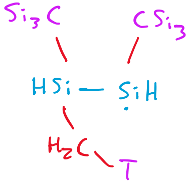

H
T·
pi bond never forms
pi bond always forms; thermal activation
R-CC·
Si3C
CSi3
Si = Si
H
H
·T
R-CC·
Si3C
CSi3
HSi:
:SiH
H2C
T
Si3C
CSi
·Si = Si
H
C3Sn·
Si3C
CSi
Si ≡ Si
C3Sn-CH2·


H₂Ċ
T
C₃Sn–CH₂•
Si₃C
CSi₃
HSi•
:SiH
H₂C
T
Si₃C
CSi
Si = Si•
H₂C
T
Si₃C
CSi₃
HSi — SiH
H₂C
T
Si₃C
CSi
Si = Si•
H₂C
T

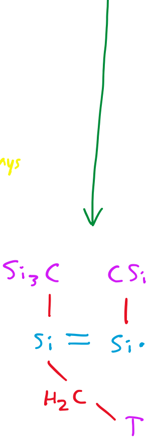
whether the methylene falls to the front or back can be guaranteed by positional control

important for ~~abstracting H~~

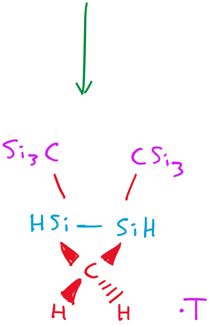
~~problem:~~ CH_2 always on "top" when on edge of crystal



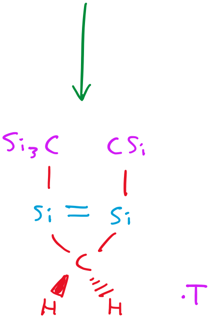
Si_3C
CSi_3
HSi — SiH
H_2C
T



Si_3C
CSi
Si = Si•
H_2C
T



Si_3C
CSi_3
HSi — SiH
C
H
H
•T

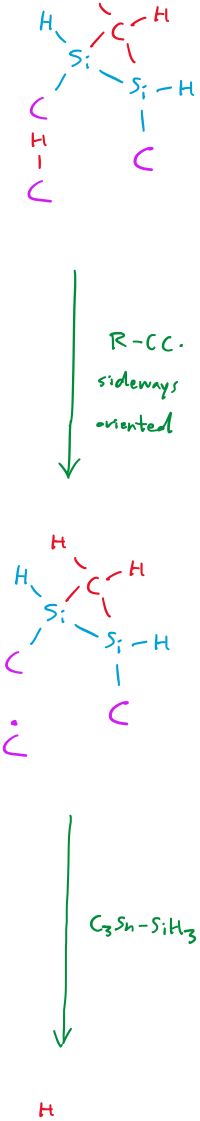


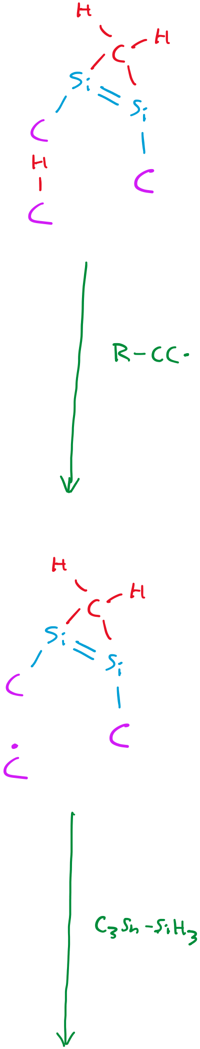
Si_3C
CSi
Si = Si
C
H
H
•T

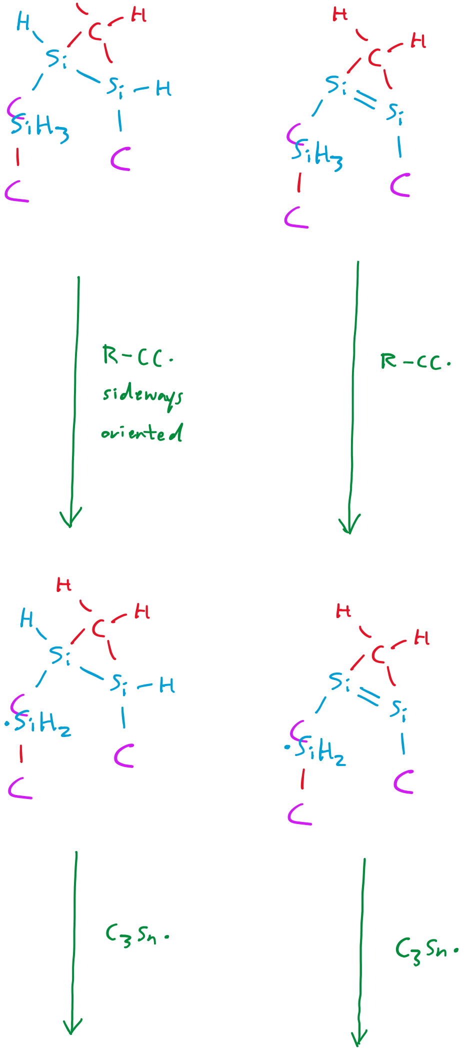
What would each of these mean?

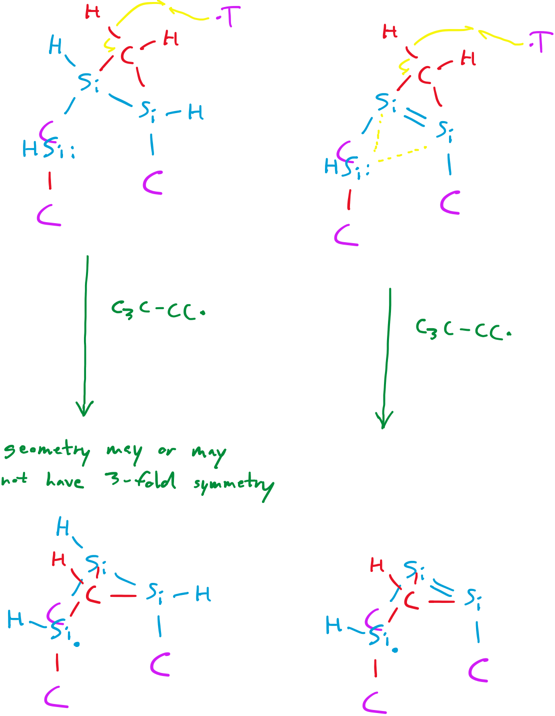
Start with layer initiation when C-H is on top

H


H
C
H
Si
Si
H
C
H
C
C
R-CC·
sideways
oriented
H
H
C
H
Si
Si
H
C
Ċ
C
C3Sn-SiH3
H


H
C
H
Si
Si
C
H
C
C
R-CC·
H
C
H
Si
Si
C
Ċ
C
C3Sn-SiH3


H
C
H
Si
Si – H
SiH3
C
C
H
C
H
Si
Si
SiH3
C
C
R–CC·
sideways oriented
R–CC·
H
H
C
H
Si
Si – H
·SiH2
C
C
H
C
H
Si
Si
·SiH2
C
C
C3Sn·
C3Sn·


·T
·T
$C_3C-CC\cdot$
$C_3C-CC\cdot$

geometry may or may not have 3-fold symmetry

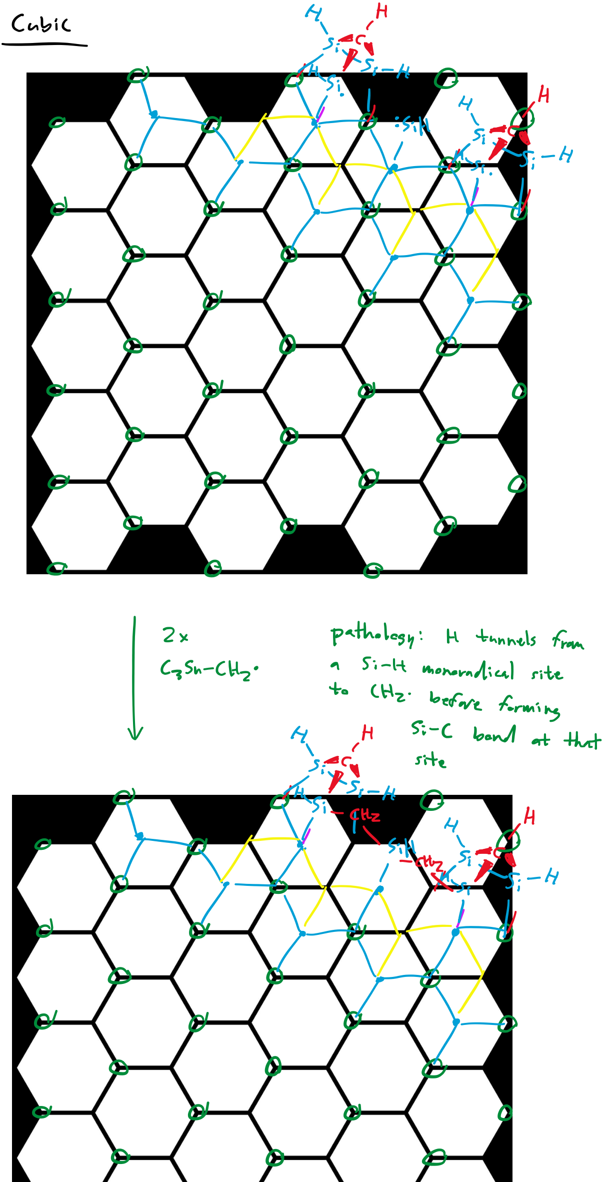
What does this mean on a slanted (111) surface?

hexagonal (111)-like problem

vs

cubic (111)-like problem

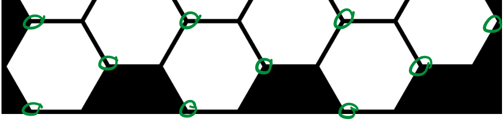
Cubic


H
H
Si
C
Si–H
H
Si
:Si–H
H
Si
C
H
Si–H
H
Si
H
H
Si
C
Si–H
H
Si
CH2
Si–H
CH2
H
Si
C
H
Si–H
H
Si

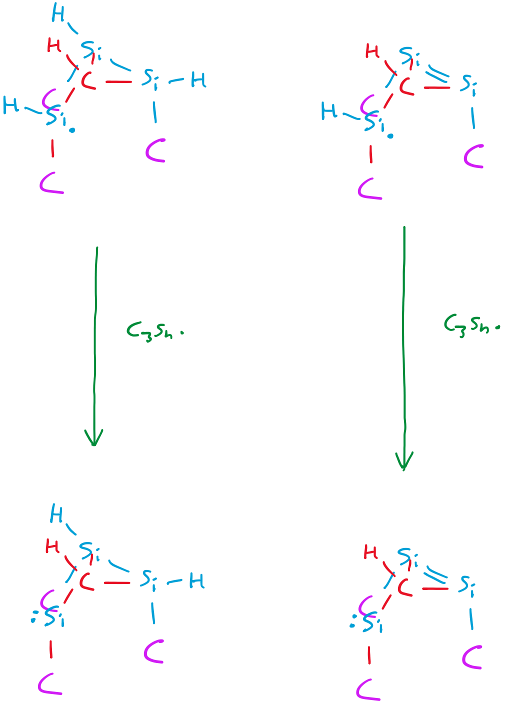
2x

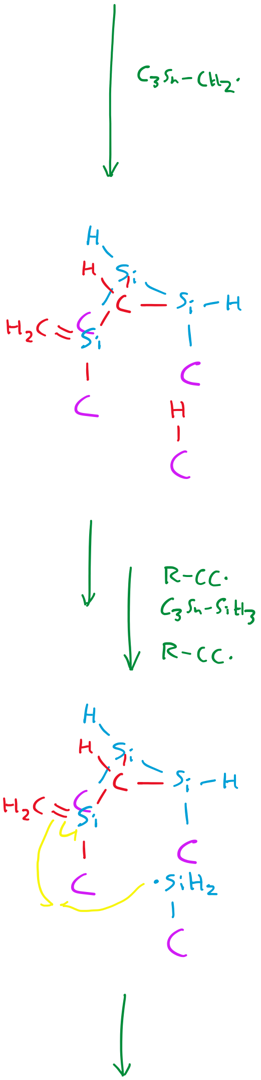
$C_3Sn{-}CH_2\cdot$

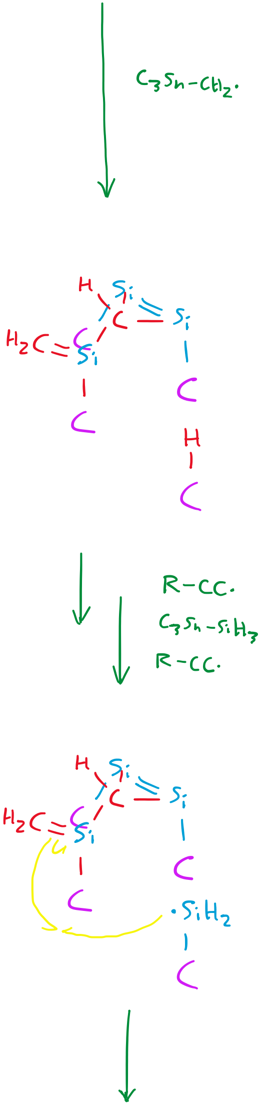
pathology: H tunnels from a Si–H monoradical site to $CH_2\cdot$ before forming Si–C bond at that site

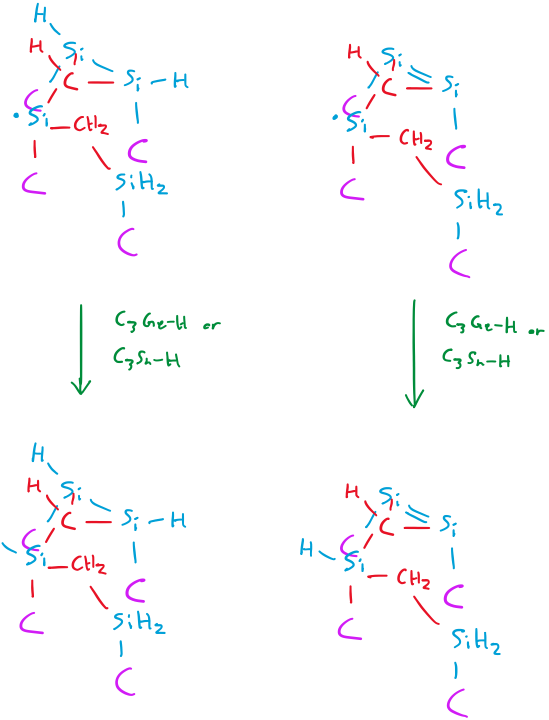


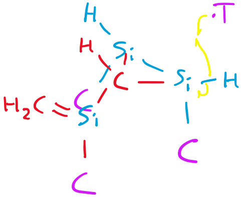
Examine Raw SiC(111) Surface More Closely

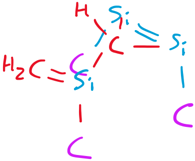


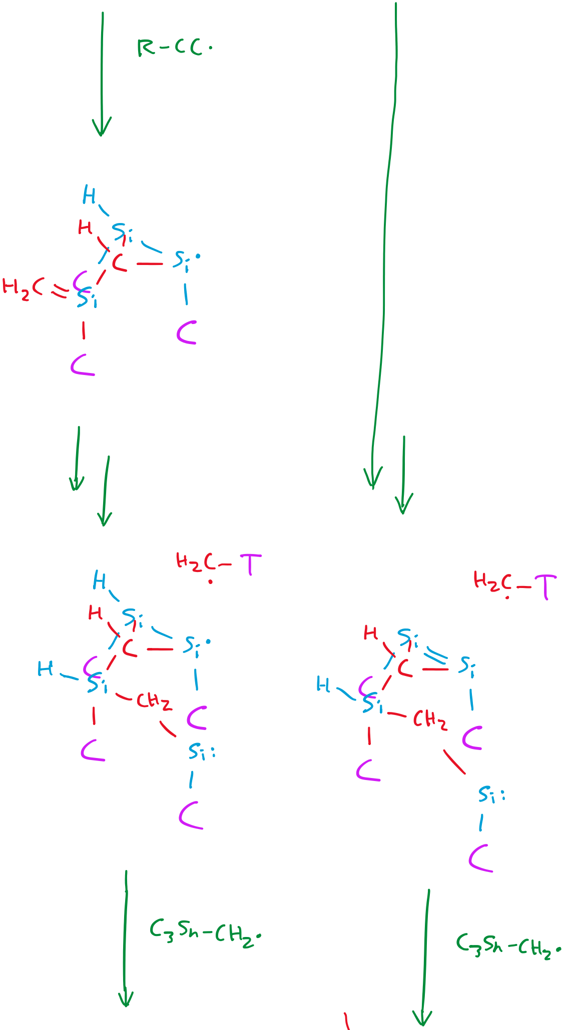

C3Sn-CH2·
H
H
Si
C
Si
H
H2C
Si
C
C
H
C
R-CC·
C3Sn-SiH3
R-CC·
H
H
Si
C
Si
H
H2C
Si
C
C
·SiH2
C

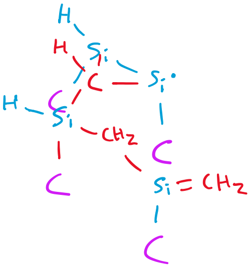

C3Sn-CH2·
H
Si
C
Si
H2C
Si
C
C
H
C
R-CC·
C3Sn-SiH3
R-CC·
H
Si
C
Si
H2C
Si
C
C
·SiH2
C


H
Si
H
C
Si
H
·Si
CH2
SiH2
C
C3Ge-H or
C3Sn-H

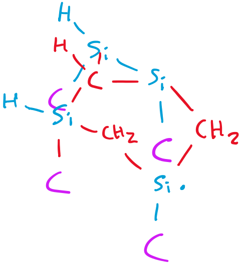

·T
H
Si
H
C
Si
H
H2C=Si
C


H
Si
C
Si
H2C=Si
C

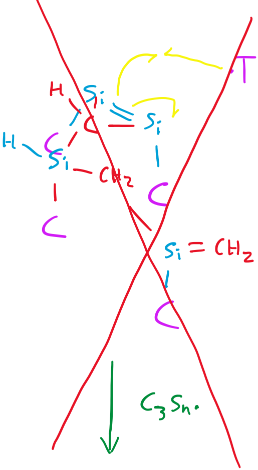

R–CC·
H2C–T
H2C–T
C3Sn–CH2·
C3Sn–CH2·



thermodynamic activation or (more likely) explicit force from inert tool

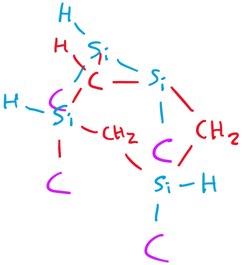


C_3Ge-H or C_3Sn-H



$C_3Sn\cdot$

illegal to apply 2 tools simultaneously


H
H
Si
C
Si
H
C
Si
CH2
CH2
C
Si
H
C
C

possibility to extend the lattice and eventually break the Si-Si bond forming a 3+5-ring

---

What to do next

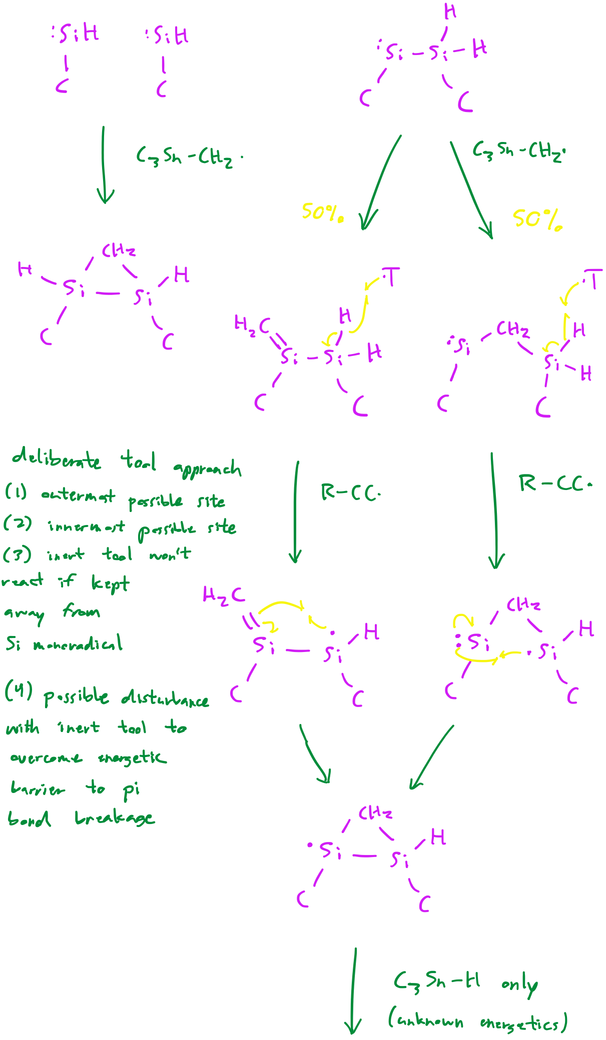
Just discovered a new possible primitive

Does not solve the (111) shrinkage problem

Formalize the primitive

Add new primitives to extend and complete
the lattice with C-H on top

Return to the (111) shrinkage problem with
more familiarity with the bond topology


:SiH
C
:SiH
C
H
:Si–Si–H
C
C
C_3Sn-CH_2·
C_3Sn-CH_2·
50%
50%
CH2
H
Si
Si
H
C
C
·T
H_2C
H
Si–Si–H
C
C
·T
:Si
CH_2
H
Si
H
C
C
R–CC·
R–CC·
H_2C
Si
Si
H
C
C
CH_2
:Si
Si
H
C
C
CH_2
·Si
Si
H
C
C
C_3Sn–H only
(unknown energetics)

deliberate tool approach

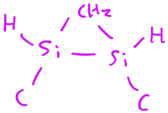
(1) outermost possible site

(2) innermost possible site

(3) inert tool won't react if kept away from Si monoradical

(4) possible disturbance with inert tool to overcome energetic barrier to pi bond breakage

assume positional control can guarantee which side the carbon lands on


CH$_2$
H
Si
Si
H
C
C

(right) by default

(left) questionable, by side the inert tool approaches from

also possible inversion (high transition state energy though)

if decomposition happens instantly, assume right Si–H monoradical won't have enough time to invert due to thermal motion

✓ plausible to assume determinism in side the CH$_2$ hangs over

Primitive 1 for SiC(111) with C–H on top

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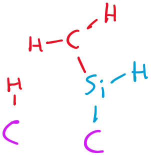
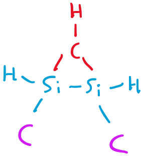
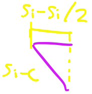
formalize how to build a lattice from this starting structure

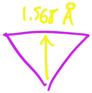



H
C
H
Si – Si
H
C
C

	Si-Si bond	Si-C bond
online model	1.356 Å	1.317 Å
paper	2.34 Å	1.95 Å
MM4	2.322 Å	1.876 Å
typical	2.33 Å	1.89 Å

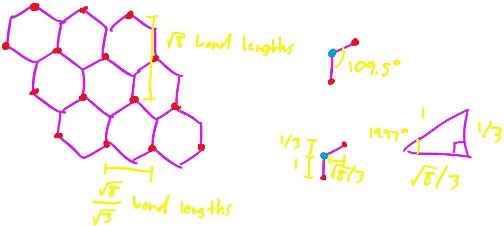
reaction coordinate = 1.568 Å





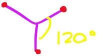
$$\text{distance} = \sqrt{(\text{Si-C})^2 - \left(\frac{\text{Si-Si}}{2}\right)^2} = 1.56\ \text{Å}$$

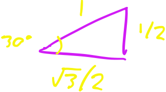
Spacing in the SiC Lattice

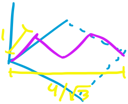

√8 bond lengths
109.5°
√8/√3 bond lengths
1/3
1
√8/3
1
19.47°
1/3
√8/3

SiC cubic lattice constant: 0.4360 nm

$$\text{bond length} = \frac{\sqrt{3}}{4} \cdot (\text{lattice constant}) = 1.89\ \text{Å}$$

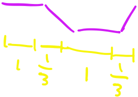




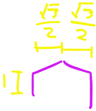


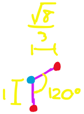
$$\cdot \text{hexagon} = \frac{1}{\sqrt{2}} \cdot \frac{4}{\sqrt{3}} = \frac{\sqrt{8}}{\sqrt{3}} \text{ bond lengths}$$

$$\cdot \text{prism} = \frac{2}{\sqrt{3}} \cdot \frac{4}{\sqrt{3}} = \frac{8}{3} \text{ bond lengths}$$



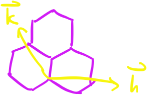
$$1 + \frac{1}{3} + 1 + \frac{1}{3} = \frac{8}{3}$$





$$\left(\frac{\sqrt{3}}{2} + \frac{\sqrt{3}}{2}\right) \cdot \frac{\sqrt{8}}{3} = \frac{\sqrt{8}}{\sqrt{3}}$$

$\vec{h} + 2\vec{k}$



$$\vec{h} = [1, 0]$$

$$\vec{k} = \left[-\frac{1}{2}, \frac{\sqrt{3}}{2}\right]$$

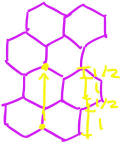
$$\vec{h} + 2\vec{k} = [0, \sqrt{3}]$$

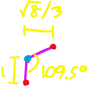
$\sqrt{3} \cdot$ hexagon spacing $= \sqrt{8}$

$\vec{h} = \sqrt{8}/\sqrt{3}$ bond lengths

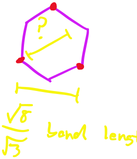
$\vec{h} + 2\vec{k} = \sqrt{8}$ bond lengths

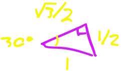
$\vec{l} = 8/3$ bond lengths



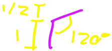


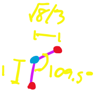
$$\left(1+\frac{1}{2}+1+\frac{1}{2}\right)\cdot\frac{\sqrt{8}}{3}=\frac{6}{2}\cdot\frac{\sqrt{8}}{3}=\sqrt{8}$$


?
√8/√3 bond lengths

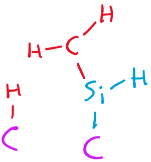


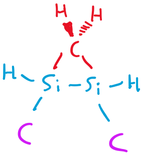
$$?=\frac{\sqrt{3}}{2}\cdot\frac{\sqrt{8}}{\sqrt{3}}=\frac{\sqrt{8}}{2}=\sqrt{2}$$ bond lengths

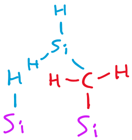


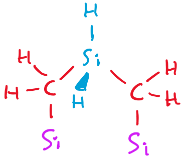


$$\left(1+\frac{1}{2}\right)\cdot\frac{\sqrt{8}}{3}=\frac{3}{2}\cdot\frac{\sqrt{8}}{3}=\frac{\sqrt{8}}{2}=\sqrt{2}$$




H
H
C
H
Si
Si
H
C
C


H
Si
H
H
H
H—C—H
Si
Si


H
Si
H
H—C
H
C—H
H
Si
Si

easiest to just fire up the old renderer in a new branch and simulate structures with xTB

Halt this project until the new renderer is finished, but using the slow diagonalization from Accelerate could be permissible

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What matters is, "can other people reproduce my code at all?"

Don't rush the high-atom-count GPU code to return to SiC build sequences either.

Implementation path: current focus

- finish renderer + migrate hardware catalog
- understand simulation requirements for protein engineering
- embed xTB binary + clean up codebase
- embed OpenMM binary
- create tutorials for just structure compilation
- create place to post & track planned speedups to simulators

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- finish SiC build sequences ← end goal
- speed up xTB & MM4
- teach others how to build atoms and simulate diamondoid nanomachines